

## 3,3'-Selenobis(propionic acid)

Khaled I. Doudin, Jon Songstad and Karl W. Törnroos\*

Department of Chemistry, University of Bergen, Allégaten 41, 5007 Bergen, Norway  
Correspondence e-mail: karl.tornroos@kj.uib.no

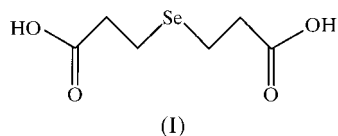
Received 6 November 2000

Accepted 22 December 2000

In contrast to  $\text{Se}[\text{CH}_2\text{C}(\text{O})\text{OH}]_2$  versus  $\text{S}[\text{CH}_2\text{C}(\text{O})\text{OH}]_2$ , the title compound,  $\text{Se}[\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OH}]_2$  or  $\text{C}_6\text{H}_{10}\text{O}_4\text{Se}$ , is structurally quite similar to its sulfur analogue. The molecule has twofold symmetry. The C—Se—C bond angle is  $96.48(8)^\circ$  and the Se—C bond lengths are  $1.9610(14)$  Å. The shortest Se···O intermolecular distance is  $3.5410(11)$  Å. The O···O distances in the carboxylic acid dimers are  $2.684(2)$  Å. The temperature dependence of the IR spectrum suggests tautomerism in the solid state.

## Comment

The crystal structure of 2,2'-selenobis(acetic acid),  $\text{Se}[\text{CH}_2\text{C}(\text{O})\text{OH}]_2$ , was reported recently (Doudin *et al.*, 2000) and shown to be very different from the structures of  $\text{X}[\text{CH}_2\text{C}(\text{O})\text{OH}]_2$ , with  $\text{X} = \text{CH}_2$  (Morrison & Robertson, 1949),  $\text{X} = \text{O}$  (Davey & Whitlow, 1973) and  $\text{X} = \text{S}$  (Paul, 1967). Whereas the latter three compounds form infinite chains through hydrogen bonds between carboxylic groups, as is common for dicarboxylic acids (Leiserowitz, 1976),  $\text{Se}[\text{CH}_2\text{C}(\text{O})\text{OH}]_2$  attains a marked *cis* configuration, forming dimers through four almost parallel hydrogen bonds. The likely cause for this dimerization is the presence of a rather strong Se···O(O—H) contact, of only  $3.081(1)$  Å, which forces one of the two acetic acid moieties of the molecule into a rare antiperiplanar conformation. In this work, we report on the structure of  $\text{Se}[\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OH}]_2$ , (I), investigating whether the apparent preference of a central Se atom to coordinate to a hydroxyl O atom also influences the structure of this compound.



The molecular structure of the title compound with the atomic numbering scheme is shown in Fig. 1. Bond lengths, angles and torsion angles are summarized in Table 1. It is evident that the structure of the title compound is essentially

similar to that of  $\text{S}[\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OH}]_2$  (Prout & Hernandez-Cassou, 1982; Vasileva *et al.*, 1992) and to the low-temperature  $\beta$ -form of 1,7-heptanedioic acid (pimelic acid; MacGillivray *et al.*, 1948); *cf.* the structure of the  $\alpha$ -form of the latter (Kay & Katz, 1958; Housty & Hospital, 1966). All these structures are composed of infinite chains of molecules linked by hydrogen bonds between the terminal carboxylic acid groups. Hence, the structural difference observed for  $\text{Se}[\text{CH}_2\text{C}(\text{O})\text{OH}]_2$  in relation to its sulfur analogue  $\text{S}[\text{CH}_2\text{C}(\text{O})\text{OH}]_2$  does not occur in the case of the  $\text{Se}[\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OH}]_2$  molecule. In this compound, the two O···O distances in a carboxylic acid dimer are equal,  $2.684(2)$  Å, and quite comparable to those observed in  $\text{S}[\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OH}]_2$ ,  $2.674(3)$  Å. The O—H···O bond angles deviate slightly from linearity,  $175(2)^\circ$ . The shortest Se···O distance,  $3.5410(11)$  Å, is to a carbonyl O atom and not to a hydroxyl O atom. Whereas the central bond angle in  $\text{S}[\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OH}]_2$ ,  $100.3(2)^\circ$  (Prout & Hernandez-Cassou, 1982), is slightly larger than in  $\text{Me}_2\text{S}$ ,  $98.8(2)^\circ$  (Hayashi *et al.*, 1989), the C—Se—C bond angle in  $\text{Se}[\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OH}]_2$ ,  $96.48(8)^\circ$ , is quite comparable to that of  $\text{Me}_2\text{Se}$ ,  $96.3(1)^\circ$  (Pandey & Dreisler, 1997). The C—Se bond lengths and all other bond lengths in  $\text{Se}[\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OH}]_2$  are as expected for this class of compounds. One may also note that all torsion angles in the sulfur and selenium compounds are quite similar; *cf.* entries in Tables 1 and 2.

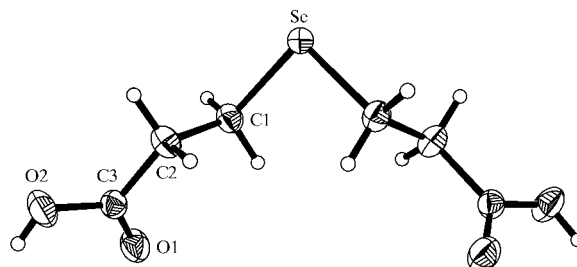


Figure 1

A view of the title compound with the atomic numbering of the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level.

Finally, some comments on the IR spectrum of  $\text{Se}[\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OH}]_2$ . It has long been known that this compound and several related ones, particularly compounds with an odd number of atoms, display a doublet for the carbonyl group (Agenäs & Lindgren, 1968; Ramsis *et al.*, 1998). At room temperature, this doublet for  $\text{Se}[\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OH}]_2$  is observed at  $1722$  and  $1685\text{ cm}^{-1}$  in Nujol, at  $1720$  and  $1697\text{ cm}^{-1}$  in KBr and at  $1712$  and  $1689\text{ cm}^{-1}$  in KBr for the dideuterated sample,  $\text{Se}[\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OD}]_2$ . At  $\sim 243\text{ K}$  in KBr, however, the intensity of the peak at  $1720\text{ cm}^{-1}$  is greatly reduced whereas the intensity of the peak at  $1697\text{ cm}^{-1}$  is significantly increased. This suggests that two configurations for  $\text{Se}[\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OH}]_2$  are present at room temperature, presumably due to tautomerism in the solid state (Sugawara & Takasu, 1999), and that the structure of the title compound represents the low-temperature  $\beta$ -form of  $\text{Se}[\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OH}]_2$ .

## Experimental

To a suspension of selenium (0.354 g, 4.5 mmol) in 1:1 THF/H<sub>2</sub>O (25 ml) was slowly added a solution of NaBH<sub>4</sub> (0.393 g, 10.0 mmol) at room temperature. After the initial red-brown colour had disappeared, the solution was warmed gently for 15 min. To the reaction mixture was then slowly added a solution of 3-bromopropionic acid (1.377 g, 9.0 mmol) and Et<sub>3</sub>N (1 g, 10 mmol) in 1:1 THF/H<sub>2</sub>O (25 ml). The solution was stirred overnight. After acidification with dilute H<sub>2</sub>SO<sub>4</sub> to pH ~2, the product was extracted with diethyl ether. The combined extracts were dried and filtered and, after removal of the solvent, a white solid remained which was crystallized from diethyl ether/pentane. The product [0.90 g (89%)] appeared as colourless thin plates with an m.p. of 421 K. The dideuterated compound, Se[CH<sub>2</sub>CH<sub>2</sub>C(O)OD]<sub>2</sub>, was prepared by repeated crystallization from D<sub>2</sub>O.

### Crystal data

C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> Se	Mo K $\alpha$ radiation
$M_r = 225.10$	Cell parameters from 8192 reflections
Orthorhombic, <i>Pbcn</i>	$\theta = 2.24\text{--}33.18^\circ$
$a = 8.5981(3) \text{ \AA}$	$\mu = 4.633 \text{ mm}^{-1}$
$b = 5.1355(2) \text{ \AA}$	$T = 253(2) \text{ K}$
$c = 18.2159(7) \text{ \AA}$	Flat prism, colourless
$V = 804.33(5) \text{ \AA}^3$	$0.33 \times 0.25 \times 0.07 \text{ mm}$
$Z = 4$	
$D_x = 1.859 \text{ Mg m}^{-3}$	

### Data collection

Bruker AXS SMART 2K CCD diffractometer	1481 independent reflections
$\omega$ scans	1149 reflections with $I > 2\sigma(I)$
Absorption correction: numerical ( <i>SHELXTL</i> ; Sheldrick 1997)	$R_{\text{int}} = 0.023$
$T_{\text{min}} = 0.296$ , $T_{\text{max}} = 0.7243$	$\theta_{\text{max}} = 33.18^\circ$
13334 measured reflections	$h = -13 \rightarrow 13$
	$k = -7 \rightarrow 7$
	$l = -26 \rightarrow 26$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2 + 0.1506P]$
$R[F^2 > 2\sigma(F^2)] = 0.023$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.061$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.150$	$\Delta\rho_{\text{max}} = 0.43 \text{ e \AA}^{-3}$
1481 reflections	$\Delta\rho_{\text{min}} = -0.54 \text{ e \AA}^{-3}$
56 parameters	Extinction correction: <i>SHELXTL</i> (Sheldrick, 1997)
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0075 (9)

The positional and isotropic displacement parameters of the hydroxy H2 atom were refined.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXTL* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Se—C1 <sup>i</sup>	1.9610 (14)	O1—C3	1.225 (2)
Se—C1	1.9610 (14)	O2—C3	1.3091 (18)
C1—C2	1.518 (2)	O2—H2	0.804 (19)
C2—C3	1.508 (2)		
C1 <sup>i</sup> —Se—C1	96.48 (8)	O1—C3—O2	124.11 (15)
C2—C1—Se	110.80 (10)	O1—C3—C2	123.02 (14)
C3—C2—C1	114.52 (12)	O2—C3—C2	112.84 (13)
C1 <sup>i</sup> —Se—C1—C2	87.04 (10)	C1—C2—C3—O1	22.4 (2)
Se—C1—C2—C3	−176.08 (11)	C1—C2—C3—O2	−159.64 (14)

Symmetry code: (i)  $-x, y, \frac{1}{2} - z$ .

**Table 2**

Selected torsion angles ( $^\circ$ ) for S[CH<sub>2</sub>CH<sub>2</sub>C(O)OH]<sub>2</sub> (Prout & Hernandez-Cassou, 1982).

C1—S—C1—C2	85.0 (2)	C1—C2—C3—O1	21.6 (2)
S—C1—C2—C3	−176.0 (2)	C1—C2—C3—O2	−160.6 (2)

This research was supported by the Norwegian Research Council through grants to KID and KWT.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1132). Services for accessing these data are described at the back of the journal.

## References

- Agenäs, L.-B. & Lindgren, B. (1968). *Ark. Kemi*, **29**, 471–477.
- Bruker (1998). *SAINT*. Version 5.00. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). *SMART*. Version 5.054. Bruker AXS Inc., Madison, Wisconsin, USA.
- Davey, G. & Whitlow, S. H. (1973). *J. Cryst. Mol. Struct.* **3**, 193–199.
- Doudin, K. I., Berge, R. K., Børve, K., Songstad, J. & Törnroos, K. W. (2000). *J. Mol. Struct.* **554**, 149–161.
- Hayashi, M., Nakata, N. & Miyazaki, S. (1989). *J. Mol. Spectrosc.* **135**, 270–283.
- Housty, J. & Hospital, M. (1966). *Acta Cryst.* **21**, 29–35.
- Kay, M. I. & Katz, L. (1958). *Acta Cryst.* **11**, 289–295.
- Leiserowitz, L. (1976). *Acta Cryst.* **B32**, 775–802.
- MacGillavry, C. H., Hoogschagen, G. & Sixma, F. L. J. (1948). *Rec. Trav. Chim. Pays-Bas*, **67**, 869–876.
- Morrison, J. D. & Robertson, J. M. (1949). *J. Chem. Soc.* pp. 1001–1008.
- Pandey, G. K. & Dreisler, H. (1997). *Z. Naturforsch. Teil A*, **32**, 482–489.
- Paul, S. (1967). *Acta Cryst.* **23**, 490–494.
- Prout, K. & Hernandez-Cassou, S. (1982). *Acta Cryst.* **B38**, 338–340.
- Ramsis, H., Ennaciri, A., Delarbre, J. L. & Maury, L. (1998). *J. Raman Spectrosc.* **29**, 331–341.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sugawara, T. & Takasu, I. (1999). *Adv. Phys. Org. Chem.* **32**, 219–265.
- Vasileva, T. P., Mozzhukhin, A. O., Antipin, M. Y. & Struchkov, Y. T. (1992). *Isv. Akad. Nauk Ser. Khim.* pp. 1766–1775.

## supporting information

*Acta Cryst.* (2001). C57, 439-440 [https://doi.org/10.1107/S0108270100021077]

## 3,3'-Selenobis(propionic acid)

Khaled I. Doudin, Jon Songstad and Karl W. Törnroos

## Computing details

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXTL* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

## 3,3'-Selenobis(propionic acid)

## Crystal data

$C_6H_{10}O_4Se$

$M_r = 225.10$

Orthorhombic, *Pbcn*

Hall symbol: -P 2n 2ab

$a = 8.5981$  (3) Å

$b = 5.1355$  (2) Å

$c = 18.2159$  (7) Å

$V = 804.33$  (5) Å<sup>3</sup>

$Z = 4$

$F(000) = 448$

? # Insert any comments here.

$D_x = 1.859$  Mg m<sup>-3</sup>

Melting point: 148° C K

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 8192 reflections

$\theta = 2.2$ – $33.2^\circ$

$\mu = 4.63$  mm<sup>-1</sup>

$T = 253$  K

Flat prism, colourless

$0.33 \times 0.25 \times 0.07$  mm

## Data collection

Bruker AXS SMART 2K CCD  
diffractometer

Radiation source: normal focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: numerical  
(*SHELXTL*; Sheldrick 1997)

$T_{\min} = 0.296$ ,  $T_{\max} = 0.724$

13334 measured reflections

1481 independent reflections

1149 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 33.2^\circ$ ,  $\theta_{\min} = 2.2^\circ$

$h = -13 \rightarrow 13$

$k = -7 \rightarrow 7$

$l = -26 \rightarrow 26$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.061$

$S = 1.15$

1481 reflections

56 parameters

1 restraint

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2 + 0.1506P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.43$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.54$  e Å<sup>-3</sup>

Extinction correction: *SHELXTL* (Sheldrick,  
1997),  $F_c^* = kFc[1 + 0.001x\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0075 (9)

Special details

**Experimental.** ? #Insert any special details here.

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Se	0.0000	0.18817 (4)	0.2500	0.02676 (8)
O1	-0.07447 (15)	0.8829 (2)	0.07928 (6)	0.0362 (3)
O2	0.13517 (14)	0.7398 (3)	0.01856 (7)	0.0379 (3)
H2	0.114 (3)	0.858 (4)	-0.0087 (12)	0.052 (6)*
C1	-0.06493 (16)	0.4425 (3)	0.17578 (8)	0.0258 (3)
H1A	-0.1455	0.3671	0.1452	0.039*
H1B	-0.1079	0.5948	0.1999	0.039*
C2	0.07177 (16)	0.5231 (3)	0.12815 (8)	0.0282 (3)
H2A	0.1548	0.5846	0.1597	0.042*
H2B	0.1099	0.3708	0.1023	0.042*
C3	0.03509 (17)	0.7322 (3)	0.07267 (9)	0.0247 (3)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Se	0.03895 (13)	0.02022 (10)	0.02111 (11)	0.000	0.00105 (8)	0.000
O1	0.0414 (6)	0.0361 (6)	0.0310 (6)	0.0112 (5)	0.0049 (5)	0.0081 (5)
O2	0.0415 (6)	0.0388 (6)	0.0333 (6)	0.0074 (5)	0.0118 (5)	0.0142 (5)
C1	0.0266 (6)	0.0274 (7)	0.0234 (6)	0.0015 (6)	-0.0004 (5)	0.0031 (5)
C2	0.0265 (6)	0.0308 (7)	0.0273 (7)	0.0005 (6)	-0.0003 (5)	0.0075 (6)
C3	0.0269 (6)	0.0254 (6)	0.0218 (6)	-0.0026 (5)	-0.0011 (5)	0.0002 (5)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Se—C1 <sup>i</sup>	1.9610 (14)	C2—H2A	0.9700
Se—C1	1.9610 (14)	C2—H2B	0.9700
C1—C2	1.518 (2)	O1—C3	1.225 (2)
C1—H1A	0.9700	O2—C3	1.3091 (18)
C1—H1B	0.9700	O2—H2	0.804 (19)
C2—C3	1.508 (2)		
C1 <sup>i</sup> —Se—C1	96.48 (8)	C3—C2—H2A	108.6
C3—O2—H2	109.9 (16)	C1—C2—H2A	108.6
C2—C1—Se	110.80 (10)	C3—C2—H2B	108.6
C2—C1—H1A	109.5	C1—C2—H2B	108.6

---

Se—C1—H1A	109.5	H2A—C2—H2B	107.6
C2—C1—H1B	109.5	O1—C3—O2	124.11 (15)
Se—C1—H1B	109.5	O1—C3—C2	123.02 (14)
H1A—C1—H1B	108.1	O2—C3—C2	112.84 (13)
C3—C2—C1	114.52 (12)		
C1 <sup>i</sup> —Se—C1—C2	87.04 (10)	C1—C2—C3—O1	22.4 (2)
Se—C1—C2—C3	-176.08 (11)	C1—C2—C3—O2	-159.64 (14)

---

Symmetry code: (i)  $-x, y, -z+1/2$ .