

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

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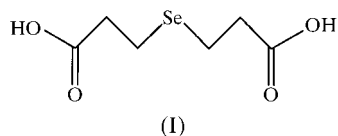
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In contrast to  $\text{Se}[\text{CH}_2\text{C}(\text{O})\text{OH}]_2$  versus  $\text{S}[\text{CH}_2\text{C}(\text{O})\text{OH}]_2$ , the title compound,  $\text{Se}[\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OH}]_2$  or  $\text{C}_6\text{H}_{10}\text{O}_4\text{Se}$ , 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.

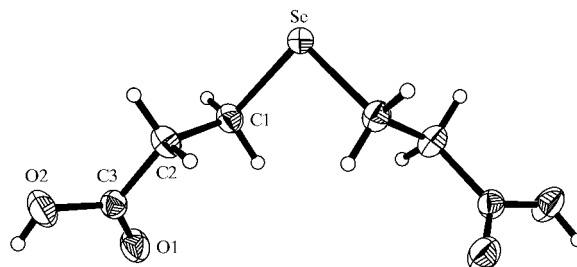


Figure 1

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)

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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.