

## Structures of 3,3'-(Selenodithio)dipropionic Acid and 3,3'-Dithiodipropionic Acid

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### Abstract

Se(SCH<sub>2</sub>CH<sub>2</sub>COOH)<sub>2</sub>,  $M_r = 289.22$ , forms monoclinic crystals, space group  $C2/c$ , with  $a = 23.283$  (17),  $b = 9.027$  (2),  $c = 4.997$  (6) Å,  $\beta = 97.09$  (6)°,  $V = 1042.28$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.843$  Mg m<sup>-3</sup>,  $F(000) = 575.98$ . The final  $R$  is 0.073 for 773 reflections. Se, located on a diad axis, is bonded to two S atoms with an Se—S bond length of 2.18 Å, and S—Se—S angle 105°. (SCH<sub>2</sub>CH<sub>2</sub>COOH)<sub>2</sub>,  $M_r = 210.26$ , is monoclinic, space group  $C2/c$ , with  $a = 5.4751$  (1),  $b = 8.8691$  (1),  $c = 18.930$  (1) Å,  $\beta = 95.800$  (8)°,  $V = 914.67$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.527$  Mg m<sup>-3</sup>,  $F(000) = 440.0$ . The final  $R$  value is 0.031 for 673 reflections. The S—S and S—C bond lengths are 2.033 (1) and 1.819 (3) Å.

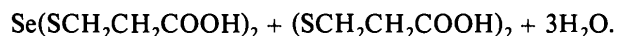
### Introduction

Interaction of Se<sup>IV</sup> compounds in aqueous acid media with mercaptocarboxylic acids (RSH) is known to produce selenotrisulphides Se(SR)<sub>2</sub> (Ganther, 1974; Holker & Speakman, 1958; Jankins, 1968), the structural elucidation of which is not available. A selenotrisulphide with RS<sup>-</sup> is derived from cysteine and has considerable biological implications. In recent years selenium has been established as an essential micronutrient and Se<sup>IV</sup> is known to be implicated initially in biological systems *via* interactions with mercapto groups, such as in cysteine and glutathione to form the corresponding selenotrisulphides. We used 3-mercaptopropionic acid (HSCH<sub>2</sub>CH<sub>2</sub>COOH) to obtain the corresponding selenotrisulphide in easily purifiable crystalline form. The crystal structure of this compound is reported in this paper and is the first of its kind of Se<sup>II</sup> mercaptocarboxylic acid complexes. As an adjunct to the study, the crystal structure of 3,3'-dithiodipropionic acid (RSSR), the other product formed during the interaction of Se<sup>IV</sup> with 3-mercaptopropionic acid is also reported.

### Experimental

#### Preparation

Selenious acid (H<sub>2</sub>SeO<sub>3</sub>) in acid medium reacts with 3-mercaptopropionic acid to give 3,3'-(selenodithio)dipropionic acid (*A*) and the disulphide (*B*) according to the scheme



Compounds *A* [Se(SR)<sub>2</sub>] and *B* (RSSR) can be readily separated by making use of the greater solubility of *B* in dilute H<sub>2</sub>SO<sub>4</sub>.

About 0.11 g (1.0 mM) of SeO<sub>2</sub> was dissolved in 25 ml of 0.5 M H<sub>2</sub>SO<sub>4</sub> and added to 0.60 g (6 mM) of 3-mercaptopropionic acid also dissolved in 25 ml of 0.5 M H<sub>2</sub>SO<sub>4</sub>. A white precipitate was immediately formed. After stirring for 1 h, 100 ml of 0.5 M H<sub>2</sub>SO<sub>4</sub> was added to the precipitate and heated on a water bath until the precipitated solids (*A* and *B*) dissolved completely. When the solution was cooled to room temperature, *A* separated as a white solid leaving *B* in solution. The compound *A* was thoroughly and repeatedly washed with 0.5 M H<sub>2</sub>SO<sub>4</sub> and then with water and air-dried.

A small amount of Se(SR)<sub>2</sub> was dissolved in 10 ml of 0.5 M H<sub>2</sub>SO<sub>4</sub> at 343 K on a water bath. On slow cooling white needle crystals of Se(SR)<sub>2</sub> separated out. Single crystals of RSSR were obtained by preparing a saturated solution in water at 343 K, followed by slow cooling. The crystals were white needles.

#### Single-crystal diffraction data

Weissenberg photographs of Se(SR)<sub>2</sub> showed the space group to be  $C2/c$ . Cell parameters and the orientation matrix were determined from 25 reflections on an Enraf–Nonius CAD-4 diffractometer. Graphite-monochromated Mo  $K\alpha$  radiation (Mo  $K\alpha_1$ ,  $\lambda = 0.70926$  Å, Mo  $K\alpha_2$ ,  $\lambda = 0.71354$  Å) was used. The

$\omega/2\theta$  scan technique was applied and 2070 reflections ( $1 < \theta < 27^\circ$ ) were collected. Of these, 987 reflections corresponded to the systematically absent reflections for the space group and 67 were used as standard-intensity-control reflections, periodically recorded during the data collection. 773 unique reflections were above the  $3\sigma(I)$  level and were used in the structure refinement. Backgrounds were measured by extending the scan range 25% on either side of the peak. Two strong reflections were recorded every second hour. No significant deterioration in intensity was noticed, the maximum fluctuation being 5%. No absorption correction was applied to the data ( $\mu = 3.83 \text{ mm}^{-1}$ ).

The same procedure as above was followed for the data collection of the *RSSR* crystal. The total reflections recorded were 1569, of which 762 corresponded to those systematically absent and 47 were the standard-intensity-control reflections. 673 reflections were used in the refinement procedures, their intensities being above  $3\sigma(I)$ . No absorption correction was necessary for this compound either,  $\mu$  being  $0.491 \text{ mm}^{-1}$ .

### Structure determination

Both structures were solved with *SHELX* (Sheldrick, 1976). Patterson maps gave the positions of the Se and S in  $\text{Se}(\text{SR})_2$ . With  $Z = 4$  and eight equivalent positions, Se atoms must occupy the special position  $(\frac{1}{4}, y, 0)$ . Difference Fourier maps based on Se and S positions showed the locations of all non-hydrogen atoms. These atoms were refined anisotropically giving an *R* factor of 0.10. At this stage the difference Fourier maps clearly showed the positions of all the H atoms. Finally all the non-hydrogen atoms were refined anisotropically and the H atoms were included with isotropic thermal parameters, giving an *R* factor of 0.073, the maximum shift/e.s.d. in any atom parameter being 0.004. The quantity minimized in the least-squares calculations was  $\sum w(|F_o| - |k_1 F_c|)^2$  and the following weighting scheme was used:  $w = k_1/[\sigma^2(F_o) + g|F_o|^2]$ , where  $k_1 = 1.0$ ,  $g = 0.0017$ .

Sharpened Patterson maps showed the S-atom positions in *RSSR*. Subsequent difference Fourier maps gave the positions of all the non-hydrogen atoms. All the atoms were refined anisotropically and the H-atom positions were obtained from a final difference Fourier map. Anisotropic refinement of all but the H atoms and isotropic refinement of H atoms gave an *R* value of 0.031. The maximum shift/e.s.d. observed for any parameter was 0.002. The weighting scheme used was the same as given above with  $k_1 = 1.0$ ,  $g = 0.0010$ .

### Results and discussion

Figs. 1 and 2 give the *ORTEP* (Johnson, 1965) plots of the  $\text{Se}(\text{SR})_2$  and *RSSR* molecules. The positional

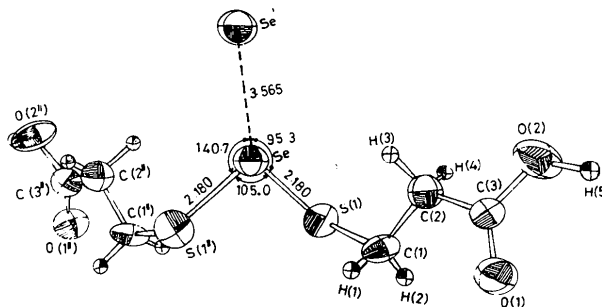


Fig. 1. The molecule of 3,3'-(selenodithio)dipropionic acid (A), showing the atom-labelling scheme and 50% probability thermal-vibration ellipsoids.

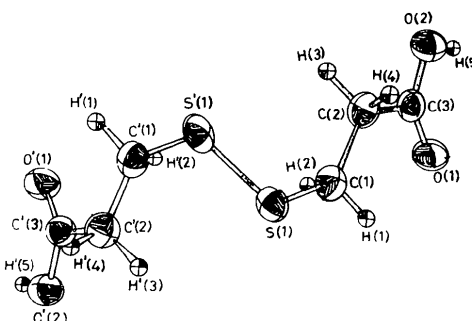


Fig. 2. The molecule of 3,3'-dithiodipropionic acid (B), showing the atom-labelling scheme and 50% probability thermal-vibration ellipsoids.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ; for H  $\times 10^3$ ) and isotropic *U* values ( $\times 10^4$ ; for H  $\times 10^3$ )

	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	<i>U</i> <sub>eq</sub> (Å <sup>2</sup> )
(I) $\text{Se}(\text{SCH}_2\text{CH}_2\text{COOH})_2$				
Se	0	1403 (1)	2500	466 (9)
S(1)	592 (1)	2871 (3)	726 (5)	516 (16)
O(1)	1942 (3)	3370 (7)	8225 (14)	642 (55)
O(2)	2265 (3)	1101 (8)	7533 (15)	548 (44)
C(1)	1118 (4)	3276 (9)	3622 (19)	419 (56)
C(2)	1469 (4)	1933 (11)	4586 (20)	441 (56)
C(3)	1906 (4)	2212 (9)	6956 (16)	373 (48)
H(1)	133 (4)	399 (11)	289 (19)	55 (27)
H(2)	88 (3)	365 (9)	493 (17)	19 (18)
H(3)	118 (4)	113 (11)	530 (21)	32 (22)
H(4)	165 (2)	158 (7)	329 (13)	15 (18)
H(5)	246 (5)	375 (13)	83 (24)	1 (19)
(II) $(\text{SCH}_2\text{CH}_2\text{COOH})_2$				
S(1)	6332 (1)	1139 (1)	7915 (<1)	487 (4)
O(1)	4642 (3)	1655 (2)	9580 (1)	512 (11)
O(2)	601 (3)	1254 (2)	9421 (1)	514 (11)
C(1)	5491 (5)	-400 (3)	8477 (1)	404 (15)
C(2)	3015 (5)	-226 (3)	8746 (1)	401 (13)
C(3)	2865 (4)	989 (3)	9288 (1)	363 (12)
H(1)	675 (4)	-43 (3)	886 (1)	46 (6)
H(2)	549 (4)	-131 (2)	822 (1)	34 (6)
H(3)	259 (4)	-114 (3)	895 (1)	51 (7)
H(4)	159 (4)	-4 (2)	836 (1)	49 (7)
H(5)	62 (5)	183 (4)	974 (1)	70 (10)

*U*<sub>eq</sub> is the average of the three eigenvalues of each anisotropic vibration tensor

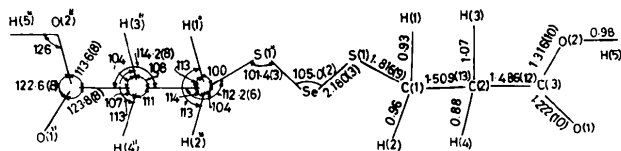


Fig. 3. Bond lengths (Å) and bond angles ( $^\circ$ ) in *A*. The e.s.d.'s range from 0.003 to 0.010 Å in bond lengths and 0.2 to 0.8 $^\circ$  in bond angles, for non-hydrogen atoms.

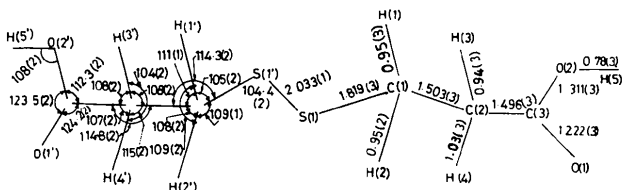


Fig. 4. Bond lengths (Å) and bond angles ( $^\circ$ ) in *B*. The e.s.d.'s range from 0.001 to 0.003 Å for non-hydrogen atoms, 0.023 to 0.034 Å for H atoms in bond lengths and 0.2 to 0.3 $^\circ$  for non-hydrogen atoms, 1.4 to 2.2 $^\circ$  for H atoms in bond angles.

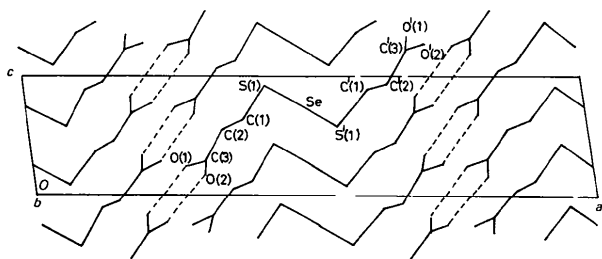


Fig. 5. A projection of the structure of *A* along the *b* axis.

Table 2. Hydrogen-bond distances (Å) and bond angles ( $^\circ$ )

	O...O	O-H	H...O	$\angle\text{O-H}\cdots\text{O}$
<i>A</i>	2.681	0.978	1.707	173.5
<i>B</i>	2.662	0.782	1.884	173.1

*A*:  $\text{Se}(\text{SCH}_2\text{CH}_2\text{COOH})_2$ ; *B*:  $(\text{SCH}_2\text{CH}_2\text{COOH})_2$ .

parameters are given in Table 1, and bond lengths and bond angles are given in Figs. 3 and 4 for the compounds  $\text{Se}(\text{SR})_2$  and  $\text{RSSR}$ . In Fig. 5 a projection of the  $\text{Se}(\text{SR})_2$  structure along the *b* axis is shown. In  $\text{Se}(\text{SR})_2$ , selenium can be regarded as in oxidation state +2, as in related selenium compounds previously reported. Table 2 gives the intermolecular hydrogen-bond parameters.\*

\* List of structure factors, anisotropic thermal parameters and least-squares-plane parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36985 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

From the results, it is clear that the Se—S linkage in  $\text{Se}(\text{SR})_2$  is similar to that found in the selenopentathionate ion  $\text{Se}(\text{SO}_3)_2^{2-}$  (Brondmo, Esperas & Husebye, 1975) in that the selenium coordination is completed by just two S atoms at a short distance and the S—Se—S angle is about 105 $^\circ$ . Both Se—S bonds per formula unit are intramolecular. Unlike these two species, a nearly planar four-coordination is exhibited in the dithiocarbonate (Brondmo, Esperas & Husebye, 1975) and dithiocarbamate complexes of  $\text{Se}^{\text{II}}$  (Husebye & Helland-Madsen, 1970), and the geometry is best considered as planar trapezoidal. Interestingly the four-coordination is obtained in different ways. In the dithiocarbonate complex the dimethyl dithiocarbonate group acts as a bidentate bridging and not a bidentate chelating ligand. One S atom from each of the dithiocarbonate groups participates as a bridging atom for the two Se atoms giving rise to two long (3.59 Å) Se—S bonds. These long Se—S bonds can be taken as secondary bonds. The terminal Se—S bonds are much shorter (2.205 Å). The dithiocarbamate group acts on the other hand as a chelating bidentate group with unequal Se—S bonds of 2.3 and 2.8 Å. In  $\text{SeBr}_2$ (tetramethylthiourea) (Wynne, Pearson, Newton & Golen, 1972; Wynne & Pearson, 1971) it is reported that selenium(II) has three-coordination with an approximately T-shaped coordination, linear Se—Br linkages of 2.57 and 2.62 Å and an Se—S linkage perpendicular to this (2.212 Å). The short Se—S distance is indicative of the strong complexation of selenium(II) with the mercapto sulphur in  $\text{Se}(\text{SR})_2$ . The oxygen of the carboxylate group in  $\text{Se}(\text{SR})_2$  is not bonded to the  $\text{Se}^{\text{II}}$ . Using the concept of hard and soft acids and bases (Pearson, 1963, 1968) one would easily classify  $\text{Se}^{\text{II}}$  along with other powerful soft acids such as  $\text{Hg}^{\text{II}}$ ,  $\text{Ag}^{\text{I}}$  and  $\text{Pd}^{\text{II}}$ . Apart from the X-ray data, an infrared study also indicates that the carboxylate group is not coordinated to  $\text{Se}^{\text{II}}$  in  $\text{Se}(\text{SR})_2$ . There are no shifts in the C=O (1700  $\text{cm}^{-1}$ ) and OH (3300–2800  $\text{cm}^{-1}$ ) frequencies and they are the same as observed in the case of the free ligand (*RSH*) and the disulphide. The SH frequency at 2600  $\text{cm}^{-1}$  observed in the free ligand (*RSH*) is absent in  $\text{Se}(\text{SR})_2$  indicating the deprotonation of the mercapto sulphur during complexation. The observed diamagnetism in  $\text{Se}(\text{SR})_2$  is explicable on the basis of Foss's (1970) interpretation of bonding in  $\text{Se}^{\text{II}}$  and  $\text{Te}^{\text{II}}$  complexes.

It is interesting to note that in  $\text{Se}(\text{SR})_2$  there is a short intramolecular contact between the S atoms of the two  $\text{RS}^-$  groups at  $x, y, z$  and  $\frac{1}{2} - x, y, -z$  of length 3.46 Å which is shorter than the van der Waals S...S contact of 3.7 Å. This accounts for the observed facile self redox decomposition of the complex according to  $\text{Se}(\text{SR})_2 \rightarrow \text{Se}^0 + \text{RSSR}$  on heating to 373 K.

The S—S and C—S bond characteristics and the Se—S—C bond angles in 3,3'-dithiodipropionic acid ( $\text{RSSR}$ ) are similar to those found for the disulphide

group in L-cystine dihydrobromide (Peterson, Steinrauf & Jensen, 1960).

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## Structure of Anthra[9,1-*cd*:10,5-*c'd'*]bis[1,2]diselenole (TSA) and of its Partially Oxidized, Metallic Polyiodide TSA I<sub>1.2</sub>

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#### Abstract

'Tetraselenaanthracene' (TSA), C<sub>14</sub>H<sub>6</sub>Se<sub>4</sub>, *M<sub>r</sub>* = 490.04, crystallizes in the monoclinic space group *P*2<sub>1</sub>/*n* with *a* = 9.318 (3), *b* = 4.111 (1), *c* = 16.035 (4) Å, β = 90.43 (2)°, *V* = 614.3 Å<sup>3</sup>, *Z* = 2, *d<sub>c</sub>* = 2.65 Mg m<sup>-3</sup>. *R* = 0.030 for 1039 observed reflections. The planar molecules form stacks along **b** with an interplanar separation of 3.59 Å. The normals to the molecular planes are inclined at 29° to the stacking axis. Short intermolecular Se–Se contacts exist between adjacent stacks, the shortest one being 3.467 (1) Å. 'Tetraselenaanthracenium iodide' (TSA I<sub>1.2</sub>), C<sub>14</sub>H<sub>6</sub>I<sub>1.20</sub>Se<sub>4</sub>, *M<sub>r</sub>* = 642.32, is monoclinic, *P*2<sub>1</sub>/*c*, with *a* = 18.644 (12), *b* = 3.856 (2), *c* = 19.746 (12) Å, β = 93.36 (5)°, *V* = 1417.1 Å<sup>3</sup>, *d<sub>c</sub>* = 3.01 Mg m<sup>-3</sup>. *R* = 0.118 for 1080 observed reflections. The structure contains two crystallographically inequivalent stacks of partially oxidized 'tetraselenaanthracenium' cations (interplanar distances

3.44 and 3.56 Å, respectively) and linear triiodide chains (proved by resonance Raman spectra) ordered in one dimension only. TSA I<sub>1.2</sub> behaves as a metal down to 220 K with σ(300 K) between 200 and 400 Ω<sup>-1</sup> cm<sup>-1</sup> measured parallel to the stacking axis.

#### Introduction

Planar organic heterocyclic molecules – especially those containing S, Se and N as ring atoms – have met with considerable recent interest in the field of materials science. Some of these compounds can be oxidized to highly conducting materials, so-called organic metals. [For recent reviews see Keller (1977), Miller & Epstein (1978), Hatfield (1979), Alcacer (1980), Carneiro (1981).] Even superconductors have been discovered recently (Bechgaard, Carneiro, Olsen, Rasmussen & Jacobsen, 1981; Bechgaard, Carneiro, Rasmussen, Olsen, Rindorf, Jacobsen, Pedersen & Scott, 1981). From a structural point of view two aspects are worth mentioning:

(i) Three-dimensional correlations between atoms of different chains should enhance the electrical con-

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