

Preparation and Crystal Structures of *cis*-Dichlorobis-(thiourea)selenium(II) and *cis*-Dibromobis(thiourea)selenium(II)

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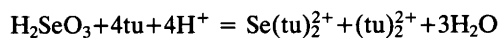
cis-Dichlorobis(thiourea)selenium(II), $\text{Se}(\text{tu})_2\text{Cl}_2$ (Fig. 1) and *cis*-dibromobis(thiourea)selenium(II), $\text{Se}(\text{tu})_2\text{Br}_2$, ($\text{tu} \equiv \text{SC}(\text{NH}_2)_2$) were prepared by reaction of Se(IV) with thiourea in strongly acidic solutions. The crystal structures were determined by X-ray methods and refined by full-matrix least-squares procedures. The structures are isomorphous, space group $P2_1/c$ (No. 14) with four formula units in the unit cell. The dichloride has the cell dimensions: $a=8.410(1)$, $b=16.522(3)$, $c=8.465(2)$ Å and $\beta=123.025(9)^\circ$. The cell dimensions of the dibromide are: $a=8.731(2)$, $b=16.868(4)$, $c=8.777(2)$ Å and $\beta=125.10(1)^\circ$.

The selenium atom has a distorted square planar environment, with long distances to halogen atoms which are *trans* to rather short bonds to sulfur atoms in thiourea. The Se-S bond lengths in $\text{Se}(\text{tu})_2\text{Cl}_2$ are 2.175(1) and 2.196(1) Å and Se...Cl distances are 3.177(1) and 3.267(1) Å. In $\text{Se}(\text{tu})_2\text{Br}_2$ the Se-S bond lengths are 2.191(2) and 2.206(2) Å and Se...Br distances are 3.261(1) and 3.335(1) Å. The Se-S bond lengths are near the expected length of a single covalent bond length, 2.18 Å. The selenium-halogen distances are much longer than the single covalent bond lengths, but shorter than van der Waals distances, 3.85 and 4.00 Å, respectively. The S-Se-S bond angle is $99.08(5)^\circ$ in $\text{Se}(\text{tu})_2\text{Cl}_2$ and $99.57(8)^\circ$ in $\text{Se}(\text{tu})_2\text{Br}_2$.

Within the errors of the determination, the thiourea groups are planar and the bond lengths are equal. The weighted mean value for the S-C bond lengths is 1.767(2) Å and for the C-N bond lengths 1.303(2) Å.

The reaction between tellurium(IV) and thiourea in acid aqueous solution, giving four coordinated complexes of divalent tellurium, is well known.¹

The corresponding reaction of selenium(IV) has not been reported. On the other hand, selenous acid has been used as test substance on the SH group in organic compounds.² In aqueous solution the thiomolecules are oxidized to disulfide while the selenium(IV) is reduced to the divalent state which disproportionates to free selenium and tetravalent selenium.³ If the solution is strongly acidic, the reduction of tetravalent selenium stops at the divalent oxidation state,⁴ e.g. in acidic solution one mol of selenous acid reacts with four mol of thiosulfate resulting in tetrathionate and selenopentathionate.⁵ In the present work, where selenous acid reacts with thiourea, the reaction should be



If the reaction goes as for the tellurium analog, the $\text{Se}(\text{tu})_2\text{X}_2$ complex is expected instead of the cation $\text{Se}(\text{tu})_2^{2+}$. In order to get information about the coordination around the selenium atom, the crystal structures were solved.

EXPERIMENTAL

Preparation of cis-dichlorobis(thiourea)selenium(II), 1.5 mmol (0.55 g) SeO_2 was dissolved in 20 ml 8 M HCl, at room temperature. A solution of 20 mmol (1.52 g) thiourea dissolved in 20 ml 8 M HCl was added under vigorous stirring. A light yellow, finely crystallized precipitate was formed. Since it was difficult to find any solvent useful for recrystallization, the mother liquor was used as follows: The temperature was slowly raised to 45 °C under continued stirring. Undissolved precipitate was removed by filtration and

the solution was set aside at 3 °C for 24 h.

Most of the crystals which deposited were identified as formamidinium disulfide dichloride. The crystals were removed from the solution and most of remaining light yellow precipitate was dissolved by heating and stirring. The solution was set aside at 3 °C for 24 h, yellow bipyramidal crystals were filtered off, washed with acetone, ether and dried in vacuum. The yield was 1.3 g or 87 % based on the amount of SeO₂ employed. The crystals were identified by X-ray methods.

Preparation of cis-dibromobis(thiourea)selenium(II), 2. Crystals of *cis*-dibromobis(thiourea)selenium(II), prepared in the same way as the corresponding dichloride compound, showed during the X-ray analysis unusual electron density around the position of the selenium atom, see the crystal data. A new product was made by dissolving 1 mmol (0.11 g) SeO₂ in 10 ml 47 % HBr, adding a solution of 4 mmol (0.31 g) of thiourea in 10 ml 47 % HBr. A yellow fine crystalline powder was formed. The solution was diluted under vigorous stirring and the temperature raised to 45 °C. Some undissolved precipitate was filtered off and the solution set aside at 3 °C for 10 h. Yellow bipyramidal crystals were

filtered off, washed with acetone, ether and dried in vacuum. The yield was 0.34 g or 88 % based on the amount of SeO₂ employed. The crystals were identified by X-ray methods.

CRYSTAL DATA

Preliminary unit cell data were obtained from Weissenberg and precession photographs. Accurate unit cell parameters were determined on an Enraf-Nonius CAD-4 diffractometer from setting angles of 25 reflections, using least-squares analysis. The reflections were automatically located and centered. The space group was determined from systematically absent reflections and confirmed by the subsequent structure analysis. The reflection data were collected with graphite monochromatized MoK α radiation. The reflections were scanned in the $\Delta\omega$ mode with variable scan rate. Of the total scan time 2/3 was used for scanning the peak and 1/3 for scanning the background on both sides of the peak. During the data collection the intensity variation with time was controlled by measuring two standard reflec-

Table 1. Crystal data and refinement characteristics.

Compound	Se(tu) ₂ Cl ₂	Se(tu) ₂ Br ₂
<i>a</i> (Å)	8.410(1)	8.731(2)
<i>b</i> (Å)	16.522(3)	16.868(4)
<i>c</i> (Å)	8.465(2)	8.777(2)
β (°)	123.025(9)	125.10(1)
<i>V</i> (Å ³)	986.2	1057.6
<i>M</i>	302.11	391.02
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
λ MoK α (Å)	0.71073	0.71073
<i>Z</i>	4	4
<i>D_x</i> (g cm ⁻³)	2.035	2.456
<i>D_{obs}</i> (g cm ⁻³)	2.00	2.47
μ (cm ⁻¹)	49.78	121.53
<i>T</i> (K)	293.0(5)	293.0(5)
<i>F</i> (000)	592	736
Sin θ/λ range (Å ⁻¹)	0–0.704	0–0.704
Scan width (°)	2.0+0.35 tg θ	1.5+0.35 tg θ
No. of refl.	3126	3380
No. of refl., <i>w</i> ≠0	1524	1327
Crystal dimensions (mm ³)	0.11×0.13×0.20	0.06×0.09×0.15
Scale factor, <i>K</i>	0.6672	1.0174
<i>R</i> (<i>F</i>)	0.044	0.039
<i>R_w</i> (<i>F</i>)	0.041	0.044
Goodness of fit	1.806	2.130
Difference Fourier max (e Å ⁻³)	0.45	0.43

tions every hour of exposure time. A control of the centering of the crystal was made at every 100th observation by the use of these two standard and two additional reflections. If any angle for any of these reflections changed by more than 0.07° , a new orientation matrix was automatically determined, using the predetermined list of reflections.

The net intensity, $I=C-TB$ and the standard deviation $\sigma(I)=(S(C+T^2B+(pI)^2))^{1/2}$ where S is the scan rate, C is the total integrated peak count, T is the ratio of scan time to background counting time, B is the background counting and p is the instability factor and was set to 0.02. The intensities were corrected for Lorentz, polarization and absorption effects. The absorption corrections were carried out by the method of Coppens.⁶ The subdivision in Gaussian points along a , b and c were $12 \times 6 \times 12$ for 1 and $6 \times 10 \times 12$ for 2.

The calculations were carried out on a PDP-11 computer using Enraf-Nonius Structure Determination Package.^{7,8} The two structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares minimizing the function $r=\sum w(F_o-KF_c)^2$, where K is a scale factor and $w=1/\sigma_{F_o}^2$. The hydrogen atoms were placed and locked in position 0.87 \AA from the nitrogen atoms and with fixed temperature factor $U=0.05$. The thiourea group was assumed to be planar and the nitrogen atoms were assumed to have a trigonal bonding system. The data for 1 and 2 showed no sign of secondary extinction.

Atomic scattering factors and anomalous dispersion values for non-hydrogen atoms were taken from Ref. 9. Crystal data and refinement characteristics are given in Table 1. A list of structure factors and anisotropic temperature factors is available from the authors on request.

Analysis of data taken from a crystal of the dibromo compound, prepared in the same way as the dichloro compound, showed a very high temperature factor for selenium. The bond distances selenium-sulfur were 2.12 and 2.13 \AA which are shorter than the single covalent bond distances, 2.18 \AA . Such an observation can probably be explained by the fact that some of the selenium positions in the crystals are occupied by sulfur. New crystals were prepared as described above.

RESULTS

From many crystal structure determinations of complexes of divalent tellurium, the configuration is known to be square planar.^{1,10} The model of the bonding is two $3c-4e$ bonding systems at right angle to each other. Each system has only two bonding electrons for the two bonds, and the bonds are rather weak. The relative length of the two bonds depends on how efficient each of the ligands uses the common bonding orbital. With a ligand where sulfur is the complexing atom or with halogen as one of the ligands, the relative strengths of the two bonds are about equal. Divalent tellurium also forms very asymmetrical complexes, *i.e.* complexes with carbon as one of the complexing atoms.¹⁰ Passing from tellurium to the less metallic element selenium, only a few structures are known, but from the known ones it seems that divalent selenium forms symmetrical bonds only when the two ligands are equal.¹¹ In the present structures with halogen in the *trans* position to sulfur the complexes are very asymmetric (Fig. 1).

Bond lengths and angles in the two crystal structures, based on the atomic coordinates in Table 2, are given in Table 3.

The environments of the selenium atoms in the two structures are given in Table 3. The Se-S bond lengths, 2.175(1) and 2.196(1) \AA in 1 and 2.191(2) and 2.206(2) \AA in 2, are equal or a little longer than the sum of the covalent radii of selenium and sulfur, 2.18 \AA . The dihedral angles SSeS/SeSC are 102.8 and 82.7° in 1 and 97.6 and 81.6° in 2. As seen from Fig. 1, the environment

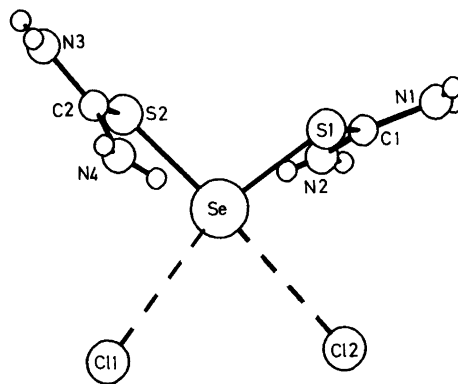


Fig. 1. ORTEP drawing of $\text{Se}(\text{tu})_2\text{Cl}_2$ as seen normal to the SeSS plane.

Table 2. Atomic coordinates for *cis*-dichlorobis-(thiourea)selenium(II) and *cis*-dibromobis-(thiourea)selenium(II). Standard deviations from least squares are given in parantheses.

Atom	x	y	z
Se(tu)₂Cl₂			
Se	0.40601(8)	0.12792(4)	0.27845(8)
C11	0.7470(2)	0.00284(8)	0.4398(1)
C12	0.7075(2)	0.23298(8)	0.6511(2)
S1	0.3022(2)	0.06922(9)	0.0091(2)
S2	0.1472(2)	0.19289(9)	0.2069(2)
C1	0.2595(7)	-0.0322(3)	0.0404(7)
C2	0.1796(7)	0.2920(3)	0.1501(6)
N1	0.2491(6)	-0.0564(3)	0.1810(6)
N2	0.2374(6)	-0.0806(3)	-0.0922(6)
N3	0.0327(6)	0.3391(3)	0.0847(6)
N4	0.3392(6)	0.3171(3)	0.1782(6)
H1	0.2278	-0.1071	0.1905
H2	0.2635	-0.0218	0.2654
H3	0.2157	-0.1319	-0.0886
H4	0.2444	-0.0616	-0.1841
H5	0.0378	0.3887	0.0536
H6	-0.0707	0.3209	0.0722
H7	0.3491	0.3664	0.1482
H8	0.4363	0.2847	0.2271
Se(tu)₂Br₂			
Se	0.4037(1)	0.12694(6)	0.2782(1)
Br1	0.7498(1)	0.00176(6)	0.4467(1)
Br2	0.7018(1)	0.23394(5)	0.6566(1)
S1	0.2940(3)	0.0714(1)	0.0081(3)
S2	0.1501(3)	0.1899(1)	0.2100(3)
C1	0.2542(11)	-0.0288(5)	0.0348(11)
C2	0.1761(11)	0.2874(5)	0.1529(9)
N1	0.2430(10)	-0.0518(4)	0.1718(9)
N2	0.2383(10)	-0.0765(5)	-0.0913(9)
N3	0.0324(10)	0.3332(4)	0.0896(10)
N4	0.3314(9)	0.3118(4)	0.1814(9)
H1	0.2219	-0.1016	0.1795
H2	0.2608	-0.0185	0.2562
H3	0.2177	-0.1267	-0.0875
H4	0.2494	-0.0585	-0.1774
H5	0.0385	0.3817	0.0596
H6	-0.0684	0.3166	0.0776
H7	0.3378	0.3602	0.1512
H8	0.0483	0.2807	0.2298

of the selenium atom in the two compounds indicates a tendency to square-planar coordination at these atoms. The Se...Cl and Se...Br contacts which occur in the *trans* position to Se-S bonds, are 3.177(1), 3.267(1) Å and

Table 3. Bond lengths (Å) and bond angles (°). Standard deviations are given in parantheses.

	Se(tu) ₂ Cl ₂	Se(tu) ₂ Br ₂
Se-S1	2.175(1)	2.191(2)
Se-S2	2.196(1)	2.206(2)
Se...X1	3.267(1)	3.335(1)
Se...X2	3.177(1)	3.262(1)
S1-C1	1.763(4)	1.769(6)
S2-C2	1.769(4)	1.772(6)
C1-N1	1.303(5)	1.320(8)
C1-N2	1.307(5)	1.308(8)
C2-N3	1.301(5)	1.296(8)
C2-N4	1.297(5)	1.297(8)
S1-Se-S2	99.08(5)	99.57(8)
X1...Se...X2	83.50(3)	84.82(2)
S1-Se...X2	85.02(4)	85.90(6)
S2-Se...X1	97.90(4)	95.54(6)
S1-Se...X1	154.94(4)	156.06(6)
S2-Se...X2	164.51(4)	163.42(6)
Se-S1-C1	105.32(15)	105.2(2)
Se-S2-C2	104.52(15)	104.6(2)
S1-C1-N1	123.3(3)	121.7(5)
S1-C1-N2	113.5(3)	114.1(5)
N1-C1-N2	123.2(4)	124.2(6)
S2-C2-N3	114.7(3)	115.2(5)
S2-C2-N4	123.0(3)	122.0(5)
N3-C2-N4	122.3(4)	122.8(6)

3.262(1), 3.335(1) Å in 1 and 2, respectively. The shortest selenium halogen contacts are *trans* to the longest Se-S bond. The S-Se...Cl angles are 154.94(4) and 164.51(4)°, and S-Se...Br angles are 156.06(6) and 163.42(6)°. The SeSSClCl and SeSSBrBr groups are approximately planar. The angles between the SeSS and SeXX planes are 25.6 and 26.0° in 1 and 2, respectively. The halogen atoms are both about one Ångström out of the SeSS plane, one on each side of the plane.

The present crystal structures can be compared with structures of selenopentathionate ions,¹²⁻¹⁴ selenium dithiocyanate¹⁵ and with the dimerized selenium trithiocyanate ion.¹⁶ The dihedral angles at Se-S in these structures are about the same as in the present structures. In selenopentathionates, the Se-S bond lengths are from 2.153(4) to 2.181(3) Å with 2.178(1) Å as weighted mean value. The angles S-Se-S are from 103.1(1) to 104.9(2)° with 103.9(1)° as the weighted mean value. There are no close contacts in the *trans* position to the Se-S bond. In

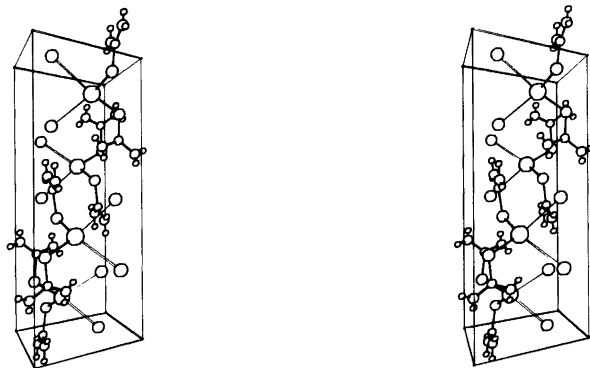


Fig. 2. A stereoscopic pair of drawings showing the content of the unit cell of $\text{Se}(\text{tu})_2\text{Cl}_2$.

$\text{Se}(\text{SCN})_2$, the Se–S bond length is 2.2136(10) Å and it has an $\text{N}\cdots\text{Se}-\text{S}$ approach of 3.000(3) Å and the angle S–Se–S is 101.59(4)°. The dimerized $\text{Se}(\text{SCN})_3^-$ ion has $\text{S}\cdots\text{Se}-\text{S}$ approaches of 2.906(3) to 3.112(3) Å with Se–S bond lengths of 2.252(2) to 2.318(3) Å and S–Se–S angles of 95.50(11) to 98.52(12)°. From the bond lengths above, the influence of the halogen atoms on the Se–S bond length in the *trans* position should be less than that of the nitrogen atom in $\text{Se}(\text{SCN})_2$. From the S–Se–S angles it can be seen that the influence is larger than from nitrogen in $\text{Se}(\text{SCN})_2$, but less than from the bridging sulfur in $\text{KSe}(\text{SCN})_3 \cdot 1/2\text{H}_2\text{O}$.

Bond lengths and angles in the thiourea groups do not deviate significantly from the values found in the crystals of thiourea itself.¹⁷ Each of the thiourea groups is planar within the experimental errors. The carbon and nitrogen are all trigonal planar in accordance with the sp^2 -hybridization of carbon atom. As seen from Table 3 the differences in the individual S–C bond lengths are not significant, nor are the differences in the individual C–N bond lengths. The weighted mean value of the S–C bond lengths is 1.767(2) Å and the weighted mean value of the C–N bond lengths is 1.303(2) Å. The N–C–N angles range from 122.3(4) to 124.2(6)° and the S–C–N angles from 113.5(3) to 123.3(3)°.

The packing in the crystals. The amino nitrogen atoms have short distances, probably involving hydrogen bonds, to halogen atoms (Table 4 and Fig. 2). The nitrogen atoms are assumed to have a trigonal planar bonding system, *i.e.* the hyd-

rogen atoms lie in or close to the planes through the thiourea group. The interatomic distances and the distances of the halogen atoms from the thiourea planes are listed in Table 4.

Table 4. The geometry of the hydrogen bonding system.

Symmetry code:

1	$1+\bar{x}, \bar{y}, 1+\bar{z}$	4	$x-1, 1/2+\bar{y}, z-1/2$
2	$1+\bar{x}, \bar{y}, \bar{z}$	5	$1+\bar{x}, 1/2+\bar{y}, 1/2+\bar{z}$
3	$1+\bar{x}, \bar{y}-1/2, 1/2+\bar{z}$	6	$x, 1/2+\bar{y}, z-1/2$

D–H \cdots A	D \cdots A [Å]	Distance from thiourea plane [Å]
N1–H \cdots C12 ₁	3.313(4)	0.147
N1–H \cdots C11 ₁	3.178(4)	–0.821
N2–H \cdots C12 ₂	3.279(4)	0.112
N2–H \cdots C11 ₃	3.194(4)	–0.939
N3–H \cdots C12 ₄	3.300(4)	–0.234
N3–H \cdots C12 ₅	3.349(4)	–0.179
N3–H \cdots C11 ₄	3.300(4)	–0.808
N4–H \cdots C12 ₅	3.186(4)	–0.179
N4–H \cdots C11 ₆	3.333(4)	1.179
N1–H \cdots Br2 ₁	3.418(6)	0.035
N1–H \cdots Br1 ₁	3.332(5)	–0.903
N2–H \cdots Br2 ₂	3.421(6)	0.166
N2–H \cdots Br1 ₃	3.343(5)	–0.925
N3–H \cdots Br2 ₄	3.442(5)	–0.281
N3–H \cdots Br2 ₅	3.535(5)	–0.108
N3–H \cdots Br1 ₄	3.451(6)	–0.878
N4–H \cdots Br2 ₅	3.335(5)	–0.108
N4–H \cdots Br1 ₆	3.451(6)	1.174

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