The Crystal Structures of the Isomorphous Methylxanthates of Divalent Sulfur and Selenium

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The crystals of sulfur and selenium di(methyl-xanthate) are isomorphous, space group $I2/c$ and have the unit cell dimensions $a = 13.580(5)$ Å, $b = 8.243(3)$ Å, $c = 18.429(4)$ Å, $\beta = 92.80(4)°$ and $a = 13.640(6)$ Å, $b = 8.299(3)$ Å, $c = 18.409(14)$ Å, $\beta = 93.56(6)°$, respectively. In both cases, the unit cell contains eight molecules.

Their structures have been determined by means of three-dimensional X-ray methods based on 712 reflection intensities above background, collected by photographic methods for the sulfur compound, and on 386 reflection intensities above background measured on a diffractometer for the selenium analogue. Least squares refinements of their structures have given conventional R-values of 0.109 and 0.052, respectively, for the former and latter compound.

In the molecules, the central sulfur and selenium atoms are bonded to two sulfur atoms, one from each of the two ligands. In addition, each central atom is weakly bonded to two sulfur atoms, one from each of two different neighbour molecules, resulting in a trapezoid planar configuration around the central atoms. Some relevant bond lengths and angles are: $S0 - S1 = 2.045(7)$ Å, $S0 - S3 = 2.059(6)$ Å, $S0 \cdots S2 = 3.625(6)$ Å, $S0 \cdots S4 = 3.709(8)$ Å and $\angle S1 - S0 - S3 = 104.2(3)°$ for sulfur di(methyl-xanthate); and $Se - S1 = 2.205(6)$ Å, $Se - S3 = 2.170(9)$ Å, $Se \cdots S2 = 3.501(9)$ Å, $Se \cdots S4 = 3.595(7)$ Å and $\angle S1 - Se - S3 = 100.8(3)°$ for the selenium analogue.

During our study of structures of divalent sulfur, selenium, and tellurium with bidentate dithio and related ligands,[1–11] three classes of structures have been found, as indicated by the three first examples in Fig. 1. Class I contains trapezoid planar four-coordinated complexes, where the central atom to ligand bonds are all intramolecular. To this class belong the structures of selenium and tellurium bis(diethyl-dithiocarbamate),[8,12] and selenium and tel-

lurium bis(4-morpholinecarbodithioate),[7,9] and the ethyl- and methylxanthates of tellurium.[6,10] Also arsenic and bismuth with phenyl substituents will bind to bidentate ligands forming class I structures.[13,14] To class II, where the trapezoid planar four-coordinated structure is based on two intramolecular and two very weak intermolecular central atom to ligand bonds, belong the structures of selenium bis(diethyldiselenophosphinate),[5] tellurium bis-(dimethyldithiophosphate),[2] and tellurium bis-(diethylthioselenophosphinate).[4] Structures of distorted square planar cis-complexes of divalent tellurium with monodentate ligands, and structures found for some positive polyhalogens also belong to this class.[15,16] Only one compound in the present study belongs to class III, which represents the trichalcogenide structure. It is the bis(dithiocarbamate) of divalent sulfur, bis(4-morpholinethiocarbonyl) trisulfide.[17] For comparison, two other structural classes are listed in Fig. 1. Structural work on trans square planar tellurium complexes with monodentate thio ligands as thiourea, shows that their structures belong to class IV.[15] In the last class, V, one finds the square planar structures of transition metals such as Ni(II), with bidentate dithio ligands.[18]

Of the structures of divalent selenium and tellurium complexes with bidentate dithio ligands, none belong to classes III—V. Steric reasons prevent them from forming complexes of class IV. However, if they were to adopt structures of class V with all four M−S bonds and all four C−S bonds being equal, both types of bonds having lengths being the average of corresponding lengths in the class I compounds above, the following angles would be found:
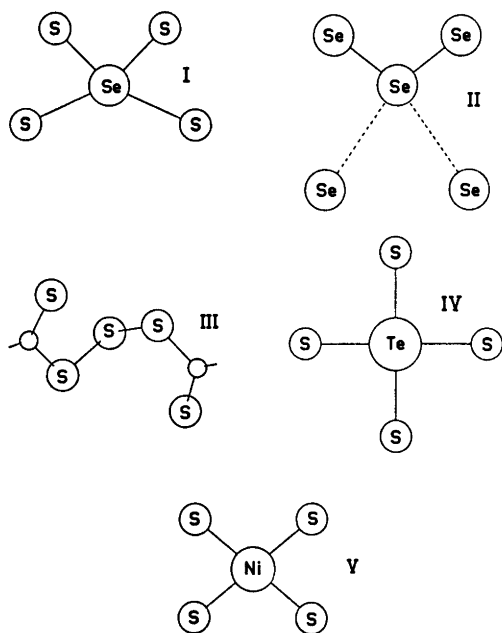
Fig. 1. Examples of the five classes of compounds I–V. Only the central atoms and their environments are shown. As representatives of the classes are chosen I: $(Et_2NCS_2)_2Se$,[8] II: $(Et_2PSe_2)_2Se$,[5] III: $OC_4H_8NC(S)S_3(S)NC_4H_8O$,[17] IV: $Te(SC(NH_2)_2)_4Cl_2.2H_2O$[15] and V: $(EtOCS_2)_2Ni$.[18] The small circles in the class III compound represent carbon atoms.

∠S—M—S intraligand with M=Se *ca.* 71°, with M=Te *ca.* 67°. ∠S—M—S interligand, with M=Se *ca.* 109°, with M=Te *ca.* 113°. In both cases, the C—S—M angles would be around 86–87°. In this discussion the S—C—S angle is assumed to be *ca.* 118°. Steric considerations, *i.e.* a combination of the small S—S bite of 2.94 Å in the ligand and the large S—M bond prevent a type IV structure being formed, and also seem to make a type V structure less likely, probably because of the two large interligand angles it would require.

In the group I compounds, the "inner" parts of the ligand sulfur *p* orbitals pointing into the S—C—S angle, overlap with *p* orbitals on the same central atom, forming a mononuclear complex.[11] The deviation from linearity and the asymmetry of the three-center four-electron S—M—S systems do not seem to influence the average S—M bond length relative to that found for the linear, symmetric three-center sys-

tems of group VI.[15] This is not expected and implies that other orbitals, probably *s*-orbitals on tellurium, also contribute to the bonding.[11] Quite recently, Mössbauer spectra have been measured for tellurium bis(dimethyldithiophosphate) and tellurium bis(diethyldithiocarbamate), and the data are interpreted as evidence for some incorporation of the tellurium $5s$ electrons in the bonding scheme.[19] For the compounds in group II, it is the "outer" part of the ligand *p* orbitals that overlap with *p* orbitals on the central atoms. Each ligand thus forms one intramolecular bond to the central atom in the molecule proper, and in addition one intermolecular weak bond to the central atom of a neighbour molecule. The three-center systems are here nearly linear and the average ligand to central atom bonds are longer than those in groups I and IV. This is expected on basis of the asymmetry in the strength of the two bonds in the linear three-center systems.[15,20]

Whether the divalent sulfur, selenium and tellurium compounds above adopt a class I, II, or III structure, seems to depend on two factors — the stronger the donor capacity of the ligand and the stronger the acceptor capacity of the central atom, the lower the group number to which the structure of the resulting compound belongs.[10]

The fact that the selenium and sulfur methylxanthates are isomorphous,[10] for the first time makes it possible to find a tendency to planar four-coordination for divalent sulfur. They are also the first xanthates of these elements whose structures have been solved.

EXPERIMENTAL

Selenium di(methylxanthate), $Se(MeOCS_2)_2$, was first made by Foss by nucleophilic substitution on the central atom of the selenopentathionate ion.[21] By an analogous procedure, we prepared sulfur di(methylxanthate), $S(MeOCS_2)_2$, from potassium pentathionate. For the present investigation, the selenium compound was made by a procedure similar to that used to prepare the diethyldithiocarbamate analogue.[8] An aqueous solution of potassium methylxanthate was added with stirring to selenious acid dissolved in 2 N hydrochloric acid in the molar ratio 4:1. The resulting oil consisting of equimolecular amounts of selenium di(methylxanthate) and the corresponding disulfide was then recrystallized from ethyl

acetate. Attempts to prepare crystals of other alkylxanthates of divalent selenium failed; in all cases the results were oily substances. Selenium di(methylxanthate) crystallized as yellow prisms, elongated along c, while the disulfide stayed in solution. The sulfur analogue gave colourless crystals of a similar shape upon recrystallization from ethyl acetate.

Crystals of the two compounds are isomorphous. From systematic extinctions, the possible space groups are $I2/c$ or Ic. ($C2/c$ or Cc if a face-centered group is preferred). The successful refinement shows that the crystals belong to the space group $I2/c$ with the eight general positions: $\pm(x,y,z; \bar{x},y,\frac{1}{2}-z; \frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z; \frac{1}{2}-x, \frac{1}{2}+y,\bar{z})$. There are eight formula units per cell. The following unit cell dimensions were found for the methylxanthate of sulfur: $a=13.580(5)$ Å, $b=8.243(3)$ Å, $c=18.429(4)$ Å and $\beta=92.80(4)°$.[10] Those for the selenium analogue are $a=13.640(6)$ Å, $b=8.299(3)$ Å, $c=18.409(14)$ Å and $\beta=93.56(6)°$.[10]

The intensity data for the sulfur compound were collected by means of the multiple-film, equi-inclination Weissenberg technique, employing Ni-filtered CuKα radiation. The crystals were unstable, and decomposed upon prolonged exposure to X-rays, even when kept in capillaries. The crystals therefore had to be changed for each layer, and the exposure time was maximum 8 h for each layer. Out of 1281 $0kl$, $1kl$ and $h0l$ through $h3l$ reflections with sin $\theta < 0.98$, only 712 were observed. The intensities of unobserved reflections were set equal to the threshold value on the visual scale.

The intensities for the selenium compound were obtained by using a Siemens AED-1 punched paper-tape-controlled single crystal diffractometer. The diffractometer was operated as a three-circle instrument using Nb-filtered MoKα radiation. Due to the rapid decomposition of the crystals as evidenced by a colour change from yellow to red, it was difficult to obtain a satisfactory set of reflection intensities. Three sets of data were taken with three different crystals. Only one of the sets, taken from a crystal mounted in a glass capillary with the c axis parallel to the spindle axis, could be used. However, out of 974 reflections with sin $\theta < 20°$, only the first 472 were later during the refinement and by comparison with short exposure films, found to be correctly measured. The final refinement of the structure is based on these reflections only. Of the latter reflections, only 386 were observed. The intensities were collected using "five-value" measurements and the $\theta - 2\theta$ scan technique with minimum scan speed 5° per min[22] with automatic setting of greater speed for the strongest reflections. Attenuation filters were automatically inserted for strong reflections to reduce counting losses. The reflections were scanned between $\theta_1 = \theta - 0.5°$ and $\theta_2 = \theta + 0.5°$ where θ is the Bragg angle for the α_1 peak. Two reference reflections were measured at intervals of 50 reflections

and reflections with intensities less than twice the standard deviation based on counting statistics, were labelled as unobserved.

Lorentz and polarization corrections were applied to the intensity data for both compounds. No correction for secondary extinction or absorption ($\mu = 95.4$ cm⁻¹) was applied to the sulfur di(methylxanthate) data, but the selenium di(methylxanthate) data was corrected for absorption ($\mu = 46.2$ cm⁻¹) by means of a program based on the Gaussian grid technique.[23] The crystal used in the latter case had the following dimensions measured as distances from a common origin to the crystal faces: 0.117 mm for 001 and 00$\bar{1}$, 0.020 mm for 110 and $\bar{1}$10 and 0.039 mm for $\bar{1}$10 and 1$\bar{1}$0. The correction was made on basis of a $8 \times 6 \times 14$ grid.

The cell dimensions for the sulfur compound were determined from NaCl-calibrated zero-layer Weissenberg films, while those for the selenium compound were calculated on basis of diffractometer measurements of a set of high-order reflections.

STRUCTURE DETERMINATIONS

The structure of the selenium compound was first to be solved. Overall scale and temperature factors were computed from a Wilson plot[24] and used in calculation of normalized structure factors for all reflections, using a program written by Shiono.[25] The resulting E statistics were slightly in favour of a centrosymmetric space group.

Phase determination for 150 reflections with $E > 1.40$ was then carried out using Long's computer program based on reiterative application of Sayre's equation.[26] The three initial reflections (10,0,4; 7,2,5; 7,4,3) produced eight possible sign sets. Two sets had a consistency index, C, equal to 1.000. $C = (|E_A \sum E_B E_C|)/(|E_A| \sum |E_B||E_C|)$ where the sum is over all terms in the Sayre equations. One of the two resulting E maps revealed most of the non-hydrogen atomic positions. All atomic positions, except those for hydrogen, were then found by a Fourier synthesis based on structure factors with contributions from the atoms above.

Since the crystals of selenium and sulfur di(methylxanthate) are isomorphous, the structure of the latter was found by assuming as a first approximation that corresponding atoms have identical coordinates in the two compounds.

Table 1. Final coordinates, in fractions of cell edges with standard deviations in parentheses.

	x	y	z
	$S(MeOCS_2)_2$		
S0	0.0903(3)	0.3542(6)	0.1464(2)
S1	0.0167(3)	0.5548(7)	0.1075(2)
S2	0.0451(3)	0.8155(7)	0.0100(3)
S3	0.1423(3)	0.4211(7)	0.2489(2)
S4	0.3159(4)	0.5623(8)	0.3182(2)
O1	0.1788(8)	0.5904(16)	0.0402(6)
O2	0.2946(7)	0.4927(15)	0.1782(5)
C1	0.0889(11)	0.6578(23)	0.0470(8)
C2	0.2459(13)	0.6709(30)	−0.0096(10)
C3	0.2597(10)	0.4988(22)	0.2447(7)
C4	0.3974(13)	0.5539(25)	0.1704(9)
	$Se(MeOCS_2)_2$		
Se	0.0876(1)	0.3371(2)	0.1464(2)
S1	0.0122(3)	0.5574(6)	0.1059(5)
S2	0.0429(4)	0.8174(6)	0.0080(5)
S3	0.1459(3)	0.4173(7)	0.2526(5)
S4	0.3214(4)	0.5638(8)	0.3189(6)
O1	0.1708(8)	0.5853(15)	0.0377(11)
O2	0.2911(9)	0.4954(14)	0.1793(14)
C1	0.0868(11)	0.6511(21)	0.0478(15)
C2	0.2391(14)	0.6647(26)	−0.0124(17)
C3	0.2632(14)	0.4967(22)	0.2473(21)
C4	0.3903(13)	0.5659(25)	0.1635(16)

Table 2. Isotropic thermal parameters $U \times 10^4$, in Å², with standard deviations in parentheses. The expression used is exp $[-8 \pi^2 U(\sin^2\theta/\lambda^2)]$.

	$S(MeOCS_2)_2$	$Se(MeOCS_2)_2$
O1	617(33)	558(42)
O2	577(30)	539(43)
C1	535(45)	412(54)
C2	793(63)	708(68)
C3	464(40)	458(61)
C4	740(57)	720(73)

Observed reflections with $K|F_c|$ larger than the observable limit, are included in the refinement with F_o put equal to the limit. Hydrogen atoms were not located and therefore not included in the refinements of the two structures (Table 1).

For selenium di(methylxanthate) the factor $R = \sum ||F_o| - |F_c||/\sum|F_o|$ converged to the value 0.20 based on all 971 reflections and isotropic temperature factors for all atoms (Table 2). At this stage of refinement, the error in the intensity data was found, and the subsequent refinements were based on the remaining 472 (including 86 unobserved) reflections. After introducing anisotropic temperature factors (Table 3) for the selenium and sulfur atoms, the R factor converged to a value of 0.054. A difference map based on the final atomic parameters gave no peaks larger than 0.5 e/Å³.

The observed structure factors for sulfur di(methylxanthate) were brought to the same

STRUCTURE REFINEMENT

The structures were both refined by a full-matrix least squares program which minimizes the quantity $r = \sum w(|F_o| - K|F_c|)^2$. Here K is a scale factor and w, the weight of a reflection, is the inverse of the variance of F_o.

Table 3. Anisotropic thermal parameters (Å² × 10⁴) in the form exp $[-2\pi^2(h^2 a^{-2} U_{11} + ... + 2hka^{-1}b^{-1} U_{12} + ...)$ with standard deviations in parentheses.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
$S(MeOCS_2)_2$						
S0	489(22)	549(39)	642(24)	−63(29)	80(26)	66(18)
S1	450(21)	665(42)	695(25)	41(29)	57(27)	78(18)
S2	685(28)	652(44)	752(29)	170(36)	114(32)	89(23)
S3	533(25)	820(46)	525(21)	−37(28)	88(27)	114(18)
S4	836(33)	1058(57)	547(23)	−20(37)	−77(30)	−48(22)
$Se(MeOCS_2)_2$						
Se	362(10)	418(13)	732(67)	−13(11)	32(22)	−45(17)
S1	443(26)	581(34)	522(133)	61(26)	72(53)	27(38)
S2	716(33)	453(35)	1429(151)	164(28)	142(54)	−30(49)
S3	467(29)	698(39)	935(159)	4(29)	39(57)	88(50)
S4	718(37)	896(49)	1194(193)	−112(36)	−80(69)	−198(58)

scale by means of comparison of common reflections for the different layers. The refinement was then started by using the same coordinates and temperature factors found for corresponding atoms in the selenium compound. The four strong reflections 20$\bar{4}$, 20$\bar{6}$, 40$\bar{2}$, and 60$\bar{6}$ had consistently much higher observed than calculated intensities. This effect cannot be explained, and the reflections were given zero weight in the final refinement cycles, but they were included in the R-factor. The R-factor reached a final value of 0.109. A final difference map revealed no peaks above 0.7 e/Å^3.

The atomic scattering factor curves used were taken from the *International Tables*.[27] Those for sulfur and selenium were corrected for anomalous dispersion, using $\Delta f'$ and $\Delta f''$ values compiled by Cromer,[28] and letting f equal the magnitude of the complex scattering factor. The calculations were carried out on an IBM 360/50H computer, using a program library made available by the Weizman Institute of Science, Rehovoth, Israel, and modified for use on the IBM computer by Dr. D. Rabinovich. The programs used to produce steering tape for the diffractometer and to produce structure factors from the output tape, were made by Mr. K. Maartmann-Moe of this Institute.

RESULTS AND DISCUSSION

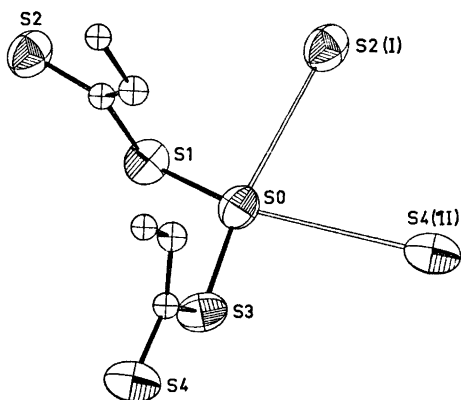The structures of the sulfur and selenium xanthate molecules are seen in Figs. 2. 3, and

Fig. 2. The structure of S(MeOCS$_2$)$_2$ and the coordination around the central atom as seen along the a axis.
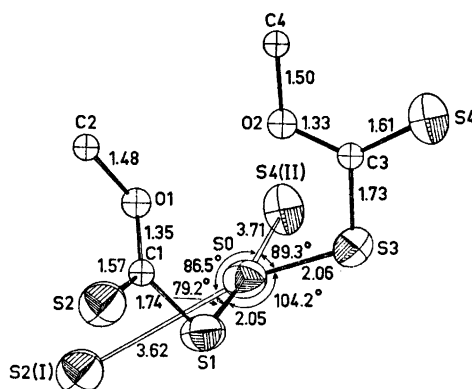
Fig. 3. The structure of S(MeOCS$_2$)$_2$ and the coordination around the central atom as seen along the b axis.

4. Weak intermolecular sulfur to central atom bonds are indicated by weaker lines. By inspection of the figures, it is seen that the structures belong to class II, mentioned above. The arrangement around the central atoms closely resembles that found around the selenium and tellurium atoms in selenium bis(diethyldiselenophosphinate) and tellurium bis(diethylthioselenophosphinate), respectively.[4,5] Thus, in the present investigation it is found that both sulfur and selenium as central atoms are bonded to four sulfur atoms in a trapezoid planar configuration. Two of these bonds are intramolecular: S0—S1 = 2.045(7) Å and S0—S3 = 2.059(6) Å for the sulfur compound: Se—S1 = 2.205(6) and Se—S3 = 2.170(9) Å for the selenium compound. These values agree well with the sum of the respective covalent radii which are 2.08 and 2.21 Å for S—S and Se—S single bonds, respectively. This indicates that the intermolecular central atom to ligand sulfur interactions *trans* to these essentially covalent bonds, must be very weak. For the sulfur compound, the lengths of these weak S0···S bonds are 3.625(6) and 3.709(8) Å. The corresponding Se—S lengths for the selenium compound are 3.501(9) and 3.595(7) Å. They may be compared to the sum of Pauling's van der Waals radii which are 3.70 and 3.85 Å for S···S and Se···S contacts, respectively.[29] From the above, it is clear that in the sulfur compound, the intermolecular S0···S interactions are of the same order of magnitude as a van der Waals contact.

Table 4. Bond lengths (Å) with standard deviations in parentheses.

$S(MeOCS_2)_2$		$Se(MeOCS_2)_2$	
S0—S1	2.045(7)	Se—S1	2.205(6)
S0—S3	2.059(6)	Se—S3	2.170(9)
S1—C1	1.74(2)	S1—C1	1.71(2)
S2—C1	1.57(2)	S2—C1	1.66(2)
S3—C3	1.73(2)	S3—C3	1.74(2)
S4—C3	1.61(2)	S4—C3	1.60(3)
C1—O1	1.35(2)	C1—O1	1.29(2)
O1—C2	1.48(2)	O1—C2	1.50(3)
C3—O2	1.33(2)	C3—O2	1.33(5)
O2—C4	1.50(2)	O2—C4	1.52(2)
S0—S2(I)	3.625(6)	Se—S2(I)	3.501(9)
S0—S4(II)	3.709(8)	Se—S4(II)	3.595(7)

Table 5. Some nonbonded intramolecular distances (Å) with standard deviations in parentheses.

S1—S2	2.839(8)	S1—S2	2.859(10)
S3—S4	2.873(7)	S3—S4	2.887(9)
S1—S3	3.238(6)	S1—S3	3.370(11)
C2—C4	3.94(2)	C2—C4	3.82(4)
O1—O2	3.03(2)	O1—O2	3.08(3)

Table 6. Bond angles (°) with standard deviations in parentheses.

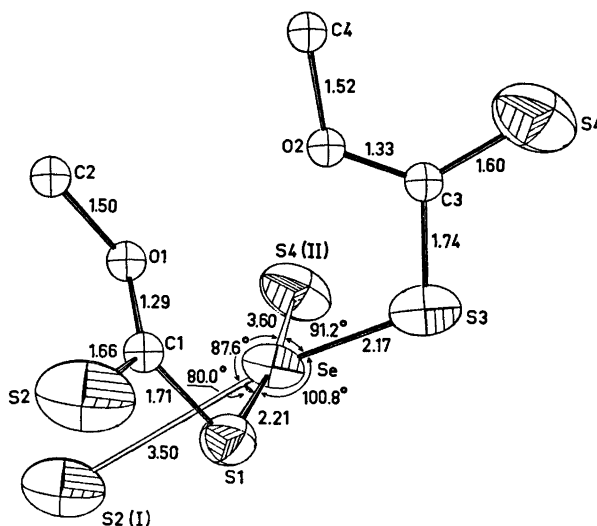| $S(MeOCS_2)_2$		$Se(MeOCS_2)_2$	
S1—S0—S3	104.2(3)	S1—Se—S3	100.8(3)
S0—S1—C1	109.7(6)	Se—S1—C1	107.8(7)
S0—S3—C3	109.3(5)	Se—S3—C3	110.6(13)
S1—C1—S2	117.9(8)	S1—C1—S2	116.3(9)
S3—C3—S4	118.7(7)	S3—C3—S4	119.9(17)
S1—C1—O1	113.5(11)	S1—C1—O1	117.7(13)
S2—C1—O1	128.6(11)	S2—C1—O1	125.9(14)
C1—O1—C2	117.3(13)	C1—O1—C2	119.5(15)
S3—C3—O2	113.7(9)	S3—C3—O2	111.6(17)
S4—C3—O2	127.6(9)	S4—C3—O2	128.5(15)
C3—O2—C4	116.8(11)	C3—O2—C4	119.2(18)
S1—S0—S2(I)	79.2(2)	S1—Se—S2(I)	80.0(2)
S3—S0—S2(I)	166.2(2)	S3—Se—S2(I)	169.5(2)
S1—S0—S4(II)	165.6(2)	S1—Se—S4(II)	167.6(2)
S3—S0—S4(II)	89.3(2)	S3—Se—S4(II)	91.2(2)
S2(I)—S0—S4(II)	86.5(2)	S2(I)—Se—S4(II)	87.6(2)
C3(II)—S4(II)—S0	89.5(7)	C3(II)—S4(II)—Se	88.4(7)
C1(I)—S2(I)—S0	101.1(6)	C1(I)—S2(I)—Se	101.8(8)

For the selenium compound, the two intermolecular Se···S distances are on the average 0.3 Å shorter than the sum of the van der Waals radii. However, the direction of the bonds and the planarity of the trapezoid MS_4 group, strongly indicate a secondary bonding interac-

tion.[30] Least squares planes through the central SOS_4 and SeS_4 groups, show that they are planar to within 0.17 and 0.14 Å, respectively (Table 8).

The difference between the structures of the methylxanthates of divalent sulfur and selenium on one side, and that of tellurium di(methyl-

Table 7. Some intermolecular contacts (Å) with standard deviations in parentheses.

	S(MeOCS$_2$)$_2$	Se(MeOCS$_2$)$_2$	Transform.
S1−C1	3.58(2)	3.51(2)	$-x, 1-y, -z$
S2−S2	3.293(8)	3.255(8)	$-x, 2-y, -z$
S2−S4	3.744(7)	3.718(12)	$\frac{1}{2}-x, \frac{3}{2}-y, \frac{1}{2}z$
S4−C1	3.59(2)	3.58(2)	
S1−S3	3.655(6)	3.672(11)	$-x, y, \frac{1}{2}-z$

Fig. 4. The structures of Se(MeOCS$_2$)$_2$ and the coordination around the central atom as seen along the *b* axis.

xanthate)[10] on the other, is pronounced. The first two belong to class II, while the latter which contains a TeS$_4$ group where all four Te−S bonds are intramolecular, belong to class I. As the ligand is the same for the three compounds, the difference in structure must be due to the difference in the acceptor capacity (electrophilicity) of the central atom. Thus, the compound with the best acceptor as central atom, here tellurium, belongs to the class with the lowest number. Divalent tellurium complexes change structural type from I to II when going from xanthate to dithiophosphate ligands, while this change for the weaker acceptor selenium, takes place between the stronger donors dithiocarbamate and xanthate.[10]

Sulfur gives here for the first time a compound where there is a tendency to planar SS$_4$ four coordination. A similar sulfur dithiocarbamate compound does not give a class II(or I) structure, but a trisulfide or class III structure.[17] The reason for this may be that with such a poor acceptor as sulfur, the tendency to four-coordination is so weak that packing effects play a large role in determining the structure.

The molecular structures of sulfur and selenium di(methylxanthate) also differ from those of the other molecules having class II structures. If one looks at the two central C−S1−M−S3−C chains in the present investigation, they both have a *cis* configuration, *i.e.* the S1−C and S3−C bonds point to the

Table 8. Least squares planes.

Equations [a]

S(MeOCS$_2$)$_2$
Plane 1: $4.630x + 4.591y + 13.634z - 4.085 = 0$
Plane 2: $-4.867x + 7.544y - 3.075z - 1.730 = 0$
Plane 3: $11.284x + 1.883y - 10.087z - 0.062 = 0$

Se(MeOCS$_2$)$_2$
Plane 1: $4.947x + 4.490y + 13.526z - 3.994 = 0$
Plane 2: $-5.425x + 7.505y - 2.386z - 1.725 = 0$
Plane 3: $11.427x + 1.874y - 10.093z - 0.039 = 0$

Distances from planes (Å)

Plane 1

Atom [b]	S1	S2	C1	O1	C2	
S(MeOCS$_2$)$_2$	0.005	0.004	−0.013	0.001	0.003	(S0 = −0.045)
Se(MeOCS$_2$)$_2$	0.002	−0.030	0.005	−0.010	0.006	(Se = −0.067)

Plane 2

Atom [b]	S3	S4	C3	O2	C4	
S(MeOCS$_2$)$_2$	−0.011	−0.004	0.018	0.006	−0.009	(S0 = 0.053)
Se(MeOCS$_2$)$_2$	0.013	0.002	−0.015	−0.014	0.014	(Se = −0.020

Plane 3

Atom [b]	S0	Se	S1	S3	S2(I)	S4(II)
S(MeOCS$_2$)$_2$	0.147	—	0.087	−0.174	−0.123	0.064
Se(MeOCS$_2$)$_2$	—	0.116	0.076	−0.140	−0.106	0.054

Interplanar angles (°)

	∠1.2	∠1.3	∠2.3
S(MeOCS$_2$)$_2$	75.66	88.49	89.72
Se(MeOCS$_2$)$_2$	76.83	87.20	92.99

[a] The equations are referred to the unit cell axes. The coefficients are adjusted so that insertion of atomic coordinates given in fractions of cell edges gives the atom's distance from the plane in Å. [b] Atoms defining plane.

same side of the plane defined by S1MS3. This is clearly seen by looking at Figs. 3 and 4. Taking selenium bis(diethyldiselenophosphinate)[5] as a representative of the other compounds with class II structures, the corresponding central P−Se−Se−Se−P chain has a *trans* configuration with Se−P bonds pointing to opposite sides of the plane defined by the three selenium atoms. Both types of analogous chains are formed by the five sulfur atoms in pentathionates.[31] The reason why the *trans* structure is preferred for selenium diseleno-

phosphinate, is that steric repulsions between ethyl groups on the two end phosphorus atoms in the chain are much reduced relative to a *cis* structure. In the methylxanthates, with only a methoxy group on each end atom of the chain, the steric repulsion in a *cis* structure is lessened, and both *cis* and *trans* configurations may be found. In both sulfur and selenium bis(methylxanthate), the ligands are planar to within 0.02 Å, and their planes make angles close to 90° with the central MS$_4$ group. The angles between the ligand planes in a molecule is near

Table 9. Some data on divalent S, Se, and Te three-centre systems. Lengths in Å, angles in degrees. M—L and M···L represent central atom to ligand bonds in the asymmetric L—M···L three-centre systems. Δ1 is the difference between these bond lengths, Δ2 and Δ3 are the differences between a single covalent bond and M—L and M···L, respectively.

Class	Compound	M—L	M···L	Δ2	Δ1	Δ3	∠L—M···L
II	Te((MeO)$_2$PS$_2$)$_2$[2]	2.440(7)	3.306(7)	0.87	0.07	0.93	173.0(3)
II	Te(Et$_2$P(S)Se)$_2$[4]	2.501(3)	3.654(5)	1.26^a		1.28	164.4(3)
I	Te(MeOCS$_2$)$_2$[10]	2.510(1)	2.846(1)	0.34	0.14	0.47	151.51(4)
		2.499(1)	2.841(1)	0.34	0.13	0.47	151.37(4)
I	Te(EtOCS$_2$)$_2$[6]	2.486(13)	2.857(16)	0.37	0.11	0.48	149.8(4)
		2.480(15)	2.897(19)	0.42	0.11	0.52	149.0(3)
I	Te(OC$_4$H$_8$NCS$_2$)$_2$[9]	2.498(7)	2.834(9)	0.34	0.12	0.46	147.4(2)
		2.530(6)	2.856(8)	0.33	0.16	0.48	147.6(2)
I	Te(Et$_2$NCS$_2$)$_2$[12]	2.519(4)	2.893(4)	0.37	0.15	0.52	145.5(1)
		2.518(4)	2.830(3)	0.31	0.14	0.46	146.4(1)
II	Se(Et$_2$PSe$_2$)$_2$[5]	2.352(2)	3.679(4)	1.33	0.01	1.34	160.8(3)
II	Se(MeOCS$_2$)$_2$[10]	2.205(6)	3.501(9)	1.30		1.30	167.6(2)
		2.170(9)	3.595(7)	1.43		1.39	169.5(2)
I	Se(OC$_4$H$_8$NCS$_2$)$_2$[7]	2.282(6)	2.791(6)	0.51	0.07	0.59	155.0(2)
		2.314(6)	2.782(5)	0.47	0.11	0.58	155.1(2)
I	Se(Et$_2$NCS$_2$)$_2$[8]	2.312(5)	2.779(5)	0.47	0.11	0.58	157.7(2)
		2.332(4)	2.719(5)	0.39	0.13	0.52	158.5(2)
I	Se(C$_4$H$_8$NCSe$_2$)$_2$[34]	2.451(1)	2.863(1)	0.41	0.11	0.52	161.37(3)
		2.449(1)	2.870(1)	0.42	0.11	0.53	161.95(3)
II	S(MeOCS$_2$)$_2$[10]	2.045(7)	3.625(6)	1.58		1.55	165.6(2)
		2.059(6)	3.709(8)	1.65		1.63	166.2(2)

^{a} M—L supposed to be a covalent Te—S bond

76° in both compounds. The bond lengths and angles found in the xanthate ligands are quite normal.[32] Each ligand sulfur atom strongly bonded to the central atom, forms a long S—C bond, ranging from 1.71—1.74 Å in the two compounds. The other S—C bonds have a higher degree of double bond character, their lengths are found between 1.57 and 1.66 Å. The O···C bond lengths range between 1.29 and 1.35 Å, demonstrating a mesomeric shift of electron density from oxygen towards the ligand sulfur atoms.

The angles on oxygen and on carbon bonded to the sulfur atoms correspond to sp^2 hybridization on these atoms. The large difference in the two S—C—O angles on sp^2 hybridized carbon, found in most xanthates may be explained on basis of VSEPR theory.[33] The average M—S—C angle is 109.4°, a relatively high value, but such high values are found in several other sulfur-containing compounds.[17]

In Table 9, structural data from structures of compounds of divalent sulfur, selenium, and tellurium with bidentate ligands belonging to

the structure classes I and II are listed. For class I compounds, the three-centre L—M···L systems are more linear for M=Se than for M=Te. The average angles are 158.2° [156.6° excluding Se(C$_4$H$_8$NCSe$_2$)$_2$[34]] and 148.6°, respectively, and can in part be explained by the difference in size of the two central atoms.[8] From the table, it is seen that the asymmetry in bond length in a three-centre system is smaller for M=Te than for M=Se, Δ1 on the average being 0.35 and 0.45 Å, respectively, for the compounds listed. If it is assumed that the compounds are essentially two-coordinate in solution with the ligands monodentate, then the new and weaker bonds forming in the solid state will be stronger for the stronger acceptor — in this case tellurium. This will thus have a weakening effect on the original strong bond *trans* to it, most so in the tellurium compounds. The Δ2 and Δ3 values tend to confirm this. Δ2, which lists the elongation of the stronger M—S bond relative to a covalent bond has as average value of 0.13 Å for M=Te and 0.11 Å for M=Se while the average Δ3 values, which
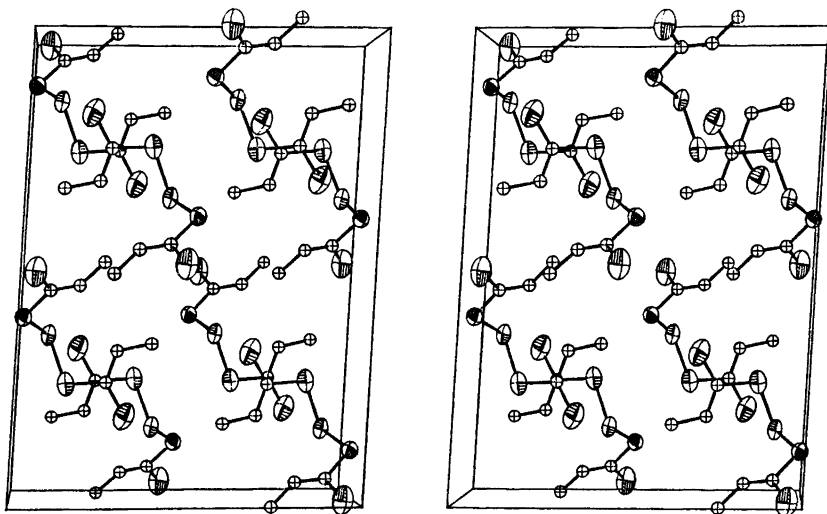
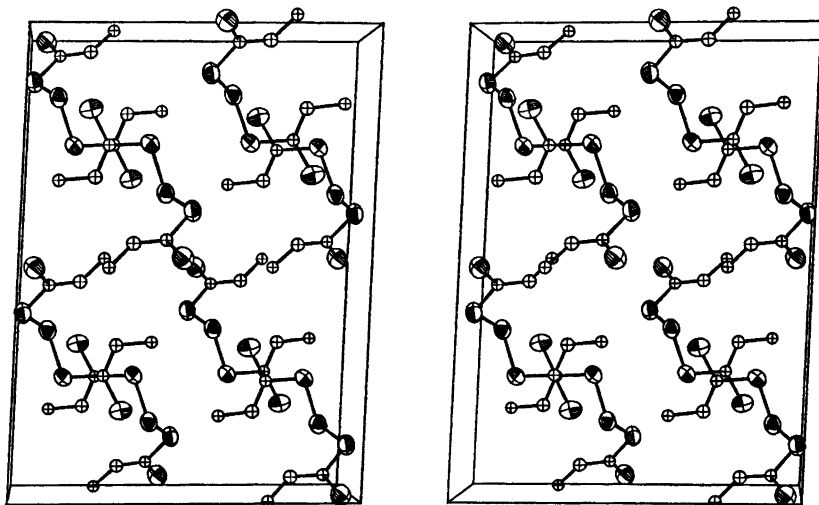*Fig. 5.* A stereoscopic drawing showing the packing of S(MeOCS₂)₂ molecules as seen along the *b* axis.

Fig. 6. A stereoscopic drawing showing the packing of Se(MeOCS₂)₂ molecules as seen along the *b* axis.

represent differences in length between weak bonds and covalent bonds are 0.48 and 0.55 Å, respectively.

Comparison between class I and class II structures, show that the latter are more linear, the L—M···L angles for the latter vary between 160.8 and 173.0°. In most class II compounds, the M···L bond is so weak that it

hardly effects the strong M—L bond *trans* to it. The latter therefore is hardly significantly different from a covalent single bond, except perhaps in Te[(MeO)₂PS₂]₂.[2] Thus the Δl values are about 0.8 Å larger in the class II than in the class I selenium and tellurium compounds.

Why do these class I and II complexes adopt a trapezoid planar configuration and not a

more symmetric one like a class V complex? The two three-centre systems, based mainly on p-orbitals require a near planar complex. When there are no restrictions on the S···S distances between donor atoms as found in tellurium complexes with monodentate thio-ligands, a square planar geometry of the central MS$_4$ group is preferred.[15] The same is found for ICl$_4^-$ and XeF$_4$,[35],[36] and the reason is that the bonding in the three isoelectronic (valence electrons) cases is based essentially on two three-centre four-electron systems at right angles to each other where only p-orbitals are involved.[15],[37–40] In the bidentate dithio ligands used, the S—S bite near 2.94 Å combined with a long average M—S bond require intraligand S—Te—S and S—Se—S angles near 66 and 70° in the class I compounds. If the resulting complex is to be symmetric, then interligand S—Se—S and S—Te—S angles of 109 and 113°, respectively, will be the result. Obviously, this configuration is not an energetically favourable one. However, with dithio ligands with larger S···S spacing, where the S—M—S intraligand angle will be permitted to reach a value close to 90°, symmetric square-planar complexes will probably be found. For the class II complexes with more linear three-centre systems, a symmetric complex require formation of a more strongly bound polymer, as found for polymeric Cu(II) complexes.[41] But with such strong bonding, it is more likely that a class I structure is adopted.

The packing of the molecules in the unit cells are vizualized in Figs. 5 and 6. There is one remarkably short intermolecular distance in both compounds, namely from S2 in the original molecule to S2 in a molecule whose transformation from the original one is $\bar{x}, 2-y, \bar{z}$. This short distance, which is 3.293(8) and 3.255(8) Å in the sulfur and selenium compound, respectively, is significantly shorter than a van der Waals contact of 3.70 Å.[29] The easy decomposition of the crystals of both compounds may be caused by disulfide formation across this short contact, followed by reduction of the central atoms to the respective elements.

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