

Preparative and X-Ray Crystallographic Data on Some Divalent Tellurium and Selenium Dithiophosphates and Dithiophosphinates

STEINAR HUSEBYE

Chemical Institute, University of Bergen, Bergen, Norway

The anions $[\text{R}_2\text{PS}_2]^-$, where R is methoxy, ethoxy, and ethyl, react with tetravalent tellurium and selenium to yield compounds of divalent tellurium and selenium. The preparation of the following compounds together with their unit cells and space groups are reported: Tellurium bis(dimethyldithiophosphate), $\text{Te}[(\text{MeO})_2\text{PS}_2]_2$; $a = 10.37 \text{ \AA}$, $b = 11.51 \text{ \AA}$, $c = 12.56 \text{ \AA}$, $Z = 4$; space group $D_{2h}^{14}\text{-}Pbcn$. Tellurium bis(diethyldithiophosphate), $\text{Te}[(\text{EtO})_2\text{PS}_2]_2$; $a = 12.75 \text{ \AA}$, $b = 21.31 \text{ \AA}$, $c = 12.64 \text{ \AA}$, $\alpha = 110.5^\circ$, $\beta = 74.5^\circ$, $\gamma = 110.5^\circ$, $Z = 6$; triclinic, space group probably $C_2^1\text{-}P\bar{1}$. Tellurium bis(diethyldithiophosphinate), $\text{Te}[(\text{Et})_2\text{PS}_2]_2$; monoclinic dimorph, $a = 12.13 \text{ \AA}$, $b = 12.71 \text{ \AA}$, $c = 12.31 \text{ \AA}$, $\beta = 116.5^\circ$, $Z = 4$; space group $C_{2h}^5\text{-}P2_1/c$. Orthorhombic dimorph, $a = 13.43 \text{ \AA}$, $b = 21.23 \text{ \AA}$, $c = 11.81 \text{ \AA}$, $Z = 8$; space group $D_{2h}^{16}\text{-}Pbca$. Selenium bis(dimethyldithiophosphate), $\text{Se}[(\text{MeO})_2\text{PS}_2]_2$; $a = 10.10 \text{ \AA}$, $b = 12.44 \text{ \AA}$, $c = 12.17 \text{ \AA}$, $\beta = 91.5^\circ$, $z = 4$; space group $C_{2h}^5\text{-}P2_1/n$. Selenium bis(diethyldithiophosphate), $\text{Se}[(\text{EtO})_2\text{PS}_2]_2$; $a = 12.30 \text{ \AA}$, $b = 12.70 \text{ \AA}$, $c = 8.46 \text{ \AA}$, $\alpha = 111.0^\circ$, $\beta = 104.5^\circ$, $\gamma = 115.5^\circ$, $Z = 2$; triclinic, space group probably $C_2^1\text{-}P\bar{1}$. Selenium bis(diethyldithiophosphinate), $\text{Se}[(\text{Et})_2\text{PS}_2]_2$; $a = 12.11 \text{ \AA}$, $b = 12.69 \text{ \AA}$, $c = 12.30 \text{ \AA}$, $\beta = 116.5^\circ$, $Z = 4$; space group $C_{2h}^5\text{-}P2_1/c$.

The stereochemistry of divalent tellurium and selenium in the compounds is discussed tentatively.

It has been shown recently^{1,2} that divalent tellurium forms complexes with a centrosymmetric square-planar, or in some cases a distorted square-planar configuration around the tellurium atom. The ligands used were mainly thiourea or substituted thioureas, alone or together with anionic ligands as halogens, pseudohalogens, or phenyl groups. A principally analogous, linear triselenium system has been found in potassium triselenocyanate.³

The purpose of this and following studies is to see if bidentate ligands will form related square-planar complexes with divalent tellurium and selenium. As bidentate ligands are chosen dithio anions as dialkyldithio-

phosphates, dialkyldithiophosphinates, dialkyldithiocarbamates, alkylxanthates, etc.

Dithio anions often function as complexing agents towards typical metal cations like those of the transition elements. Complexes of the first two types of anions mentioned above, have been known only for a relatively short time. Dithiophosphate metal complexes have been reported mostly in connection with analytical and spectral studies.⁴⁻⁶ Extensive preparative work on metal dithiophosphinates, thioselenophosphinates and diselenophosphinates have recently been reported by Kuchen *et al.*⁷⁻¹⁰ Dithiocarbamate and xanthate complexes have been known for quite a long time and spectral and structural studies have been performed on some of these, especially the nickel (II) complexes.^{4,11-17}

X-Ray structural work has been done on nickel (II) complexes with diethyldithiophosphate,¹⁴ ethylxanthate,¹⁷ dipropyldithiocarbamate,¹⁵ and diethyldithiocarbamate.¹⁶ The three first complexes have been shown to have a square-planar NiS_4 group, with the nickel atom in a centre of symmetry. The diethyldithiocarbamate complex is also centrosymmetric,¹⁶ and further structural work may reveal a square-planar NiS_4 configuration also there.

The square-planar structures of these nickel(II) complexes indicate the possibility of the same dithio anions giving square-planar complexes also with divalent tellurium and selenium.

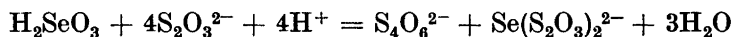
There have been several reports on divalent tellurium and selenium dialkyldithiophosphates, dialkyldithiocarbamates, and xanthates. Busev and Min-T'iao Huang¹⁸ prepared selenium bis(diethyldithiophosphate) and Busev and others^{6,18,19} report the use of diethyldithiophosphates for analytical determination of tetravalent tellurium and selenium. Foss²⁰⁻²⁴ has prepared and studied some divalent tellurium and selenium dithiocarbamates and xanthates. So far, however, no structure work except unit cell and space group determinations for two of the divalent tellurium xanthates seems to have been done.²⁴

Some predictions of the structures of divalent tellurium and selenium compounds with dithio anions might *a priori* be possible. By comparison with structures of similar divalent nickel complexes and structures of divalent tellurium and selenium complexes with unidentate sulphur-containing ligands, the compounds would be expected to be square-planar or distorted square-planar. The Te—S and Se—S bond lengths would be expected to be longer than single covalent bonds as found for the corresponding complexes with unidentate ligands.^{1,3}

The non-bonded sulphur-sulphur distance in the dithio anions mentioned here is somewhat small for both sulphur atoms to coordinate to the same central atom. Especially a tellurium atom with a covalent radius of 1.37 Å²⁵ may not fit into such a mononuclear square-planar complex. However, in the case of dithiophosphates and dithiophosphinates where the spacing is largest, only small adjustments of bonds and angles should be necessary. On the other side, a small non-bonded sulphur-sulphur distance might lead to polymeric structures or to rather large differences in the lengths of the two Te—S or Se—S bonds from the same anion as found in the trivalent antimony²⁶ and arsenic²⁷ xanthates.

SYNTHESIS

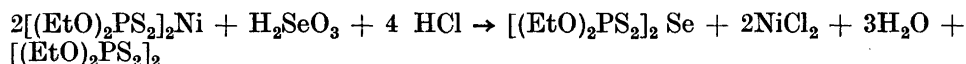
More than sixty years ago, Norris and Fay^{28,29} found that tetravalent tellurium and selenium react with sodium thiosulphate in acid solution to yield monotelluro- and monoselenopentathionates. The reaction is:



with a corresponding equation for tellurium. Tellurium and selenium are reduced to the divalent state in these reactions.^{20,21}

Russel³⁰ reported that the reaction between tetravalent selenium and alkali dithiocarbamates gave dithiocarbamates of tetravalent selenium but that the result was often an equimolecular mixture of the divalent selenium dithiocarbamate and the corresponding bis(thiocarbamyl) disulphide. Tetravalent tellurium dithiocarbamates are also labile with respect to rearrangement into the divalent dithiocarbamate and the corresponding disulphide.²³

Recently Busev showed a corresponding reduction of tetravalent selenium upon reaction with diethyldithiophosphates:^{18,31}



The present work has shown that alkali dithiophosphates and dithiophosphinates reduce tetravalent tellurium and selenium to the divalent state in analogy with the above.

The compounds described below were prepared by adding aqueous solutions of the alkali dithiophosphates and dithiophosphinates to hydrochloric acid solutions of Te(IV) or Se(IV) at room temperature. Orange to yellow oils then separated out and usually solidified rapidly. The solid consisting of the divalent compound and the corresponding disulphide was then in most cases dissolved in the alcohol corresponding to the substituent alkyl- or alkoxy groups. Upon cooling, the crystalline divalent tellurium and selenium compounds were obtained while the disulphides stayed in solution.

EXPERIMENTAL

Preparation of salts. Dimethyl- and diethyldithiophosphonic acids were prepared according to the procedure of Fletcher *et al.*³² by bringing phosphorus pentasulphide and the corresponding alcohol in the molar ratio 1:4 to react in benzene under reflux. Potassium dimethyldithiophosphate was isolated by adding alcoholic potassium hydroxide to the benzene solution of the acid.³³ Ammonium diethyldithiophosphate was obtained on introduction of gaseous ammonia.

Sodium dimethyl- and diethyldithiophosphinates were prepared from the respective tetraalkyl diphosphine disulphides^{34,35} by heating them with equivalent amounts of crystalline sodium sulphide and sulphur.³⁶ In the case of the dimethyldithiophosphinate, the mixture had to be heated above 205°C for a clear solution to form. This was probably the reason for the low yield (21 %) obtained.

Preparation of the tellurium compounds. These were prepared by dissolving 0.01 mole of tellurium dioxide in 5 ml hot, concentrated hydrochloric acid. After cooling to room temperature, 15 ml of water was added. To this solution, 0.04 moles of alkali dithiophosphate or dithiophosphinate dissolved in 15–20 ml of water, was added slowly, with stirring. Immediately, yellow to orange oils separated out and solidified rapidly. The solution was decanted off and the solid mass was washed with the corresponding cold alcohol. The solid containing the divalent tellurium dithiophosphate or dithio-

Table 1. Analytical data on the crystalline tellurium and selenium compounds.

Compound	Found	Calc.	Yield %	M.p., °C.
Te[(MeO) ₂ PS ₂] ₂	Te 28.96	Te 28.87	79.9	90.5–91.5 *
Se[(MeO) ₂ PS ₂] ₂	Se 19.97	Se 20.08	62.4	61–62
Te[(EtO) ₂ PS ₂] ₂	Te 25.49	Te 25.62	75.7	65–66 *
Se[(EtO) ₂ PS ₂] ₂	Se 17.51	Se 17.57	61.1	87–88 **
Te[(Et) ₂ PS ₂] ₂	Te 28.30	Te 29.40	88.0	99–100
Se[(Et) ₂ PS ₂] ₂	S 33.75	S 33.28	78.9	116–117 *

* Decomp.

** Busev and Min-T'iao Huang¹⁸ report a melting point of 81–82°C for this compound.

phosphinate and the corresponding disulphide was then dissolved in the corresponding warm alcohol or another suitable solvent such as benzene. Upon cooling, the tellurium compound crystallized out while the disulphide stayed in solution.

Preparation of the selenium compounds. The preparations were analogous to those of the tellurium compounds; in these cases 0.01 mole of selenious acid dissolved in 20 ml 2 N hydrochloric acid was used. In the case of the dimethyldithiophosphate compound, the oil did not solidify. After washing the oil several times with cold methanol, it was dissolved in hot methanol and crystallization then took place upon cooling.

Analysis. The tellurium compounds and especially the selenium compounds were not quite stable in solutions. When kept in the solid state in a refrigerator, the compounds were stable for months.

Tellurium and selenium bis(dimethyldithiophosphate) were apparently amorphous, and especially the tellurium compound was very little soluble. Attempts at recrystallization resulted in decomposition or failed to give single crystals. After thorough washing in warm benzene the melting points (decomp.) were found to be about 196°C and 125°C, respectively. (Found: S 34.76. Calc. for C₄H₁₂P₂S₂Te: S 34.26. Found: S 39.40. Calc. for C₄H₁₂P₂S₂Se: S 39.30). The high melting points and low solubility of these compounds may be due to polymerization. The corresponding tellurium and selenium bis(dimethyldithiocarbamates)²² are also insoluble and have high melting points.

In Table 1, the analyses and yields of the crystalline compounds are listed. The melting points are uncorrected, and an asterisk indicates that decomposition started before melting took place. These compounds were soluble in most organic solvents. The phosphinates were less soluble than the phosphates, especially in polar solvents.

CRYSTAL DATA

Unit cells and space groups were determined from single-crystal oscillation and Weissenberg photographs. Copper radiation with $\lambda = 1.5418 \text{ \AA}$ was used and the calculated parameters are probably accurate within 0.5 %. Densities were obtained by flotation in aqueous salt solutions.

Tellurium bis(dimethyldithiophosphate), Te[(CH₃O)₂PS₂]₂. Crystallization from methanol yielded orange to red prisms {110} elongated along the *c* axis, with $a = 10.37 \text{ \AA}$, $b = 11.51 \text{ \AA}$, $c = 12.56 \text{ \AA}$. There are four formula units per unit cell; density, calc. 1.94, found 1.92 g/cm³. The space group, from systematic absences, is D_{2h}^{14} -*Pbcn*. Reflections hkl with $h + k = 2n + 1$ are systematically weak, and this together with four molecules and eight general positions in the cell, indicates twofold symmetry of the molecules, with the tellurium atoms on twofold axes.

Tellurium bis(diethyldithiophosphate), $\text{Te}[(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2]_2$. Deep orange red, triclinic crystals from ethanol. They were large, somewhat poorly developed prisms along c with forms $\{010\}$, $\{100\}$ and probably $\{110\}$. The cell dimensions are, $a = 12.75 \text{ \AA}$, $b = 21.31 \text{ \AA}$, $c = 12.64 \text{ \AA}$, $\alpha = 110.5^\circ$, $\beta = 74.5^\circ$, $\gamma = 110.5^\circ$ with six formula units in the cell. Density, calc. 1.67, found 1.66 g/cm^3 . The triclinic space group, from morphology, probably is $C_1^1-P\bar{1}$.

Tellurium bis(diethyldithiophosphate), $\text{Te}[(\text{C}_2\text{H}_5)_2\text{PS}_2]_2$. Two types of crystals could be distinguished: Yellow prisms and needles (A) separated out from ethanol, while orange plates (B) separated out from a 1:1 mixture of ethanol and dioxane. Unit cells and space groups were determined for both types.

A. The prisms and needles were elongated along $[101]$, with $a = 12.13 \text{ \AA}$, $b = 12.71 \text{ \AA}$, $c = 12.31 \text{ \AA}$, $\beta = 116.5^\circ$. There are four formula units per unit cell; density, calc. 1.69, found 1.71 g/cm^3 . The crystals were twins, and the systematic absences were therefore not quite clear, but isomorphism with the corresponding selenium compound was indicated. The space group is then probably $C_{2h}^5-P2_1/c$.

B. The crystal chosen for investigation was an almost quadratic, flat plate $\{001\}$. Unit cell dimensions are, $a = 13.43 \text{ \AA}$, $b = 21.23 \text{ \AA}$, $c = 11.81 \text{ \AA}$. There are eight formula units per cell; density, calc. 1.71, found 1.72 g/cm^3 . The space group, from systematic absences, is orthorhombic $D_{2h}^{15}-Pbca$.

Selenium bis(dimethyldithiophosphate), $\text{Se}[(\text{CH}_3\text{O})_2\text{PS}_2]_2$. Yellow, monoclinic prisms from methanol, elongated along a . The cell dimensions are, $a = 10.10 \text{ \AA}$, $b = 12.44 \text{ \AA}$, $c = 12.17 \text{ \AA}$, $\beta = 91.5^\circ$. There are four formula units in the cell; density, calc. 1.71, found 1.70 g/cm^3 . From systematic absences, the space group is $C_{2h}^5-P2_1/n$.

Selenium bis(diethyldithiophosphate), $\text{Se}[(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2]_2$. Yellow prisms from ethanol, elongated along c with forms $\{100\}$ and $\{010\}$. The cell dimensions are, $a = 12.30 \text{ \AA}$, $b = 12.70 \text{ \AA}$, $c = 8.46 \text{ \AA}$, $\alpha = 111.0^\circ$, $\beta = 104.5^\circ$, $\gamma = 115.5^\circ$. There are two formula units in the unit cell; density, calc. 1.51, found 1.49 g/cm^3 . The space group is triclinic, and from morphology probably $C_1^1-P\bar{1}$.

Selenium bis(diethyldithiophosphate), $\text{Se}[(\text{C}_2\text{H}_5)_2\text{PS}_2]_2$. Light yellow transparent prisms from benzene. The crystals are monoclinic and isomorphous with type A of the corresponding tellurium compound, and were like these elongated along $[101]$. There is no twinning here, and the cell constants are nearly identical with $a = 12.11 \text{ \AA}$, $b = 12.69 \text{ \AA}$, $c = 12.30 \text{ \AA}$, $\beta = 116.5^\circ$. There are four formula units in the cell, with density, calc. 1.51, found 1.48 g/cm^3 . The space group, from systematic absences, is $C_{2h}^5-P2_1/c$.

DISCUSSION

The unit cell and space group data yield little definite information about possible structures of the compounds. Tellurium bis(dimethyldithiophosphate) probably has twofold symmetry with the tellurium atom on twofold axis. But there is no indication of centrosymmetrical square-planar structures from these data.

An X-ray structure analysis of one of the compounds, tellurium bis(dimethyldithiophosphate), is being completed. Molecules $(\text{CH}_3\text{O})_2\text{P}-\text{S}-$

$\text{Te}-\text{P}(\text{OCH}_3)_2$ can be distinguished. However, the thiono sulphur atoms $\begin{array}{c} \parallel \\ \text{S} \end{array}$

form weak intermolecular bonds to tellurium atoms in neighbouring molecules. Distorted square-planar TeS_4 groups thus occur in the resulting polymeric system.

Acknowledgement. The author wishes to express his thanks to Professor Olav Foss for his advice and suggestions during this work.

REFERENCES

1. Foss, O. *Acta Chem. Scand.* **16** (1962) 779.
2. Foss, O., Husebye, S. and Marøy, K. *Acta Chem. Scand.* **17** (1963) 1806.
3. Foss, O. and Hauge, S. *Acta Chem. Scand.* **17** (1963) 1807.
4. Jørgensen, C. K. *J. Inorg. Nucl. Chem.* **24** (1962) 1571, and references cited therein.
5. Busev, A. I. and Ivanyutin, M. I. *Zh. Anal. Khim.* **11** (1956) 523, cited in *Z. Anal. Chem.* **158** (1957) 39.
6. Bode, H. and Arnsward, W. *Z. Anal. Chem.* **185** (1962) 179.
7. Kuchen, W. and Metten, J. *Angew. Chem.* **72** (1960) 584.
8. Kuchen, W., Metten, J. and Judat, A. *Chem. Ber.* **97** (1964) 2306.
9. Kuchen, W. and Knop, B. *Angew. Chem.* **76** (1964) 496.
10. Kuchen, W. and Knop, B. *Angew. Chem.* **77** (1965) 259.
11. Chatt, J., Duncanson, L. A. and Venanzi, L. M. *Suomen Kemistilehti B* **29** (1956) 75.
12. Cotton, F. A. and McCleverty, J. A. *Inorg. Chem.* **3** (1964) 1398.
13. Krebs, H., Weber, E. F. and Fassbender, H. *Z. anorg. allgem. Chem.* **276** (1954) 134.
14. Gilinskaya, E. A. and Porai-Koshits, M. A. *Kristallografiya* **4** (1959) 241.
15. Peyronel, G. *Z. Krist.* **103 A** (1941) 157.
16. Shugam, E. A. and Shkol'nikova, L. M. *Kristallografiya* **3** (1958) 749.
17. Franzini, M. *Z. Krist.* **118** (1963) 393.
18. Busev, A. I. and Min-T'iao Huang *Zh. Neorgan. Khim.* **7** (1962) 88.
19. Busev, A. I. and Ivanyutin, M. I. *Komis. Analit. Khim., Akad. Nauk. SSSR, Inst. Geokhim. i Analit. Khim.* **11** (1960) 172.
20. Foss, O. *Acta Chem. Scand.* **3** (1949) 435.
21. Foss, O. *Acta Chem. Scand.* **3** (1949) 708.
22. Foss, O. *Acta Chem. Scand.* **3** (1949) 1385.
23. Foss, O. *Acta Chem. Scand.* **7** (1953) 226.
24. Foss, O. *Acta Chem. Scand.* **11** (1957) 1442.
25. Pauling, L. *The Nature of the Chemical Bond*, 3rd. Ed., Cornell University Press, Ithaca, New York 1960.
26. Gottardi, G. *Z. Krist.* **115** (1961) 451.
27. Carrai, G. and Gottardi, G. *Z. Krist.* **113** (1960) 373.
28. Norris, J. T. and Fay, H. *Am. Chem. Journ.* **23** (1900) 119.
29. Norris, J. T. and Fay, H. *J. Am. Chem. Soc.* **28** (1906) 1675.
30. Russel, W. F. *U. S. Pat.* 2,347,128 (1944).
31. Busev, A. I. *Talanta* **11** (1964) 485.
32. Fletcher, J. H., Hamilton, J. C., Hechenbleikner, I., Hoegberg, E. I., Sertl, B. J. and Cassaday, J. T. *J. Am. Chem. Soc.* **72** (1950) 2461.
33. Ketelaar, J. A. A. and Gersmann, H. R. *Rec. Trav. Chim.* **77** (1958) 973.
34. Reinhardt, H., Bianchi, D. and Mölle, D. *Chem. Ber.* **90** (1957) 1656.
35. Kuchen, W., Buchwald, H., Strolenberg, K. and Metten, J. *Ann.* **652** (1962) 28.
36. Kuchen, W., Strolenberg, K. and Metten, J. *Chem. Ber.* **96** (1963) 1733.

Received February 27, 1965.

Acta Chem. Scand. **19** (1965) No. 5