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Zelinskii Institute of Organic Chemistry,
Academy of Sciences of the USSR

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NEW ASPECTS OF THE CHEMISTRY OF COMPLEXES OF SELENIUM AND TELLURIUM

D. I. Ryabchikov and I. I. Nazarenko

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I. INTRODUCTION

The growing interest in the chemistry of rare and dispersed elements, which include selenium and tellurium, is connected with the development of new branches of technology — automation, telemechanics, and semiconductor technology.

In the Periodic System selenium and tellurium lie between sulphur, a typical non-metal, and polonium, a metal. This position determines the most important physical and chemical properties of these elements. As regards electrical conductivity, tellurium recalls a metal while selenium is a semiconductor. Selenium and tellurium and their compounds are widely used in semiconductor technology for the production of thermoelements, systems for stabilising temperature, and in radio technology.

Because of its high resistivity and its ability to pass current only in one direction, selenium is used as a rectifier. Its electrical conductivity increases 1000 times on exposure to light and on this is based its use in the production of photometers and photoelectric cells. Selenium is also used as a luminophore in the manufacture of screens permitting a high resolution, in radar systems, television receivers, and other apparatus. In metallurgy, addition of selenium and tellurium to cast iron, steels, and other alloys improves the structure and workability of these materials, and raises the hardness and strength of the alloys. Selenium is also used in the rubber industry as a catalyst for organic synthesis, and in the glass industry.

In spite of the considerable scale of world production of selenium (845 tonnes in 1959, excluding the USSR) the demand for it in semiconductor technology is still not satisfied. The consumption of selenium in other branches of industry is gradually decreasing [*sic* (Ed. of Translation)] and the need for new sources for the production of selenium and tellurium arises more clearly; the possibility of finding substitutes for selenium is also being studied.

In the USSR, the problem of a complete and rational separation of these elements on an enormous scale, from sulphide ores containing selenium and tellurium, is very substantial.

The wide use of selenium and tellurium in semiconductor technology creates new problems as regards their preparative and analytical chemistry. For semiconductors these elements and their compounds are required in a super-pure state. In analytical chemistry problems arise in the development of rapid and accurate methods for determining selenium and tellurium in various materials — mineral raw material, semiconductors, steels, alloys, etc.

Methods of obtaining pure selenium, tellurium, and their compounds have been discussed by Novoselova, Pashinkin, and Popovkin[1].

A number of new analytical methods for determining selenium and tellurium have been described in recent years.

The reaction of selenium with 3,3′-diaminobenzidine was first mentioned[2] in 1948, but a number of papers on the use of this highly sensitive and specific reaction for the determination of selenium in various types of material have appeared in the last two or three years. A new, very sensitive reagent for the determination of tellurium — Bismuthol-II — was proposed in 1960–1961.[3,4] A series of papers on the reaction of tellurium with thiourea appeared in 1957–1962. There is a very large amount of published work on tellurium complexes. Apart from the long-known acido-complexes with hydrogen halides (M_2TeX_6 type), complexes of tellurium with nitrogen- and sulphur-containing ligands have been examined.

A study of the compounds of selenium and tellurium shows that these elements often differ sharply in their properties: tellurium forms a large group of complexes, whereas only isolated examples of selenium complexes are known. The difference in the ability of these elements to form complexes opens up great possibilities of analytical chemistry in the development of sensitive and specific methods for their determination.

An attempt is made in this review to generalise from the diverse, and often contradictory, publications, mainly in recent years, on complexes of selenium and tellurium and their application to preparative and analytical chemistry. The properties of the simple compounds are not discussed; regarding them see, for example, Kudryavtsev[18] and Brasted[19].

1. Hydrogen Halogeno-Acids of Selenium and Tellurium and Their Salts

For tellurium, hydrogen halogeno-acids of composition $TeCl_4.HCl.5H_2O$, $TeBr_4.HBr.5H_2O$, and $TeI_4.HI.8H_2O$, obtained by the action of the corresponding acids on $TeCl_4$, are known[20,21]. They are formed as needle-shaped prisms, the chloride being yellow, the bromide red, and the iodide black. They are very hygroscopic and easily deliquesce in the air, and on heating they easily lose a molecule of HX.

The oxide fluorides $TeF_4.3TeO_2.6H_2O$, $TeF_4.TeO_2.2H_2O$, and $TeF_4.TeO_2.H_2O$, for which the existence of the complex anion $[TeO_2F_2]^{2-}$ is proposed, have also been described[20,22].

When CsF was added to a solution of TeF_4 in HF the compound $CsTeF_5$ was obtained[23]. Other pentafluorotellurates(IV), $NH_4TeF_5.H_2O$, $KTeF_5$, and $Ba(TeF_5)_2.2H_2O$, are also known.

A compound with oxine, $HTeI_5.2Oxin.10H_2O$, was isolated from a solution in HI containing tellurium[24].

Aynsley[25] obtained a fluoro-complex of tellurium and pyridine $[C_5H_5NH]TeF_5$ and a series of halogeno-complexes with urea $[CON_2H_5]TeX_5$, where X = Cl, Br, I.[26]

In the compounds with urea the stability of the $[TeX_5]^-$ anion increases from the chloro- to the iodo-complex, since the chloro-complexes are easily converted into the bromo- and iodo-complexes under the action of the corresponding HX. Several authors were unable to obtain fluoro--complexes with urea.

Numerous hexahalogenotellurates(IV) are known — with the chlorides, bromides, and iodides of K, Rb, and Cs,[27,28] and also the chlorides and bromides of ammonium and thallium[29–31].

However, it has so far not been shown definitely that the free hexahalogeno-acids of Te^{IV} can be obtained. Some authors[32] state that $H_2TeCl_6.2H_2O$ can be obtained as well--formed yellow crystals by dissolving freshly precipitated TeO_2 in HCl (1 : 1), and that these give H_2TeBr_6 on reaction with HBr.

Dobrowolski[29,30] and Yakovleva and Troitskii[33] attempted to reproduce Ripan's experiments[32]. However, the hexahalogeno-acids of tellurium could not be obtained by him. Dobrowolski[29,30] obtained the ammonium and thallium salts $(NH_4)_2TeCl_6$ and Tl_2TeBr_6.

The stability of compounds containing $[TeX_6]^{2-}$ ions apparently depends to a considerable extent on the degree of polarisation caused by the cation. The strongly polarising hydrogen ion therefore makes the $[TeX_6]^{2-}$ anion unstable, and this may explain the instability of acid solutions containing the coloured $[TeI_6]^{2-}$ ion[34–36]. It is therefore possible to agree with Dobrowolski[29,30] who doubts the possibility of isolating H_2TeCl_6 and H_2TeBr_6 in the pure state. It is clear that for the same reason the hexahalogenotellurates(IV) of lithium and sodium were not obtained, as these are cations which also possess a high polarising power. On the other hand, large weakly polarising cations — K^+, NH_4^+, Tl^+, Rb^+, Cs^+ — form quite stable hexa-chloro-, -bromo-, and -iodo-tellurates(IV).[27–31]

H_2SeBr_6 was isolated in the pure state from hydrogen halogeno-acids of selenium[37,38]. This acid dissolves in

water without decomposition but decomposes in air with liberation of bromine and colloidal selenium. The analogous hydrogen hexachloroselenate(IV) has not been obtained. The compounds $SeO_2.2HCl$ and $SeO_2.2HBr$ were shown to be identical with the hydrates $SeOCl_2.H_2O$ and $SeOBr_2.H_2O$.[39]

Potassium and ammonium hexachloroselenates(IV) were obtained as yellow crystalline materials which decompose easily in the air[40]. $(NH_4)_2SeBr_6$, K_2SeBr_6, and Rb_2SeBr_6 are also known[27,41].

Examination of solutions containing compounds of selenium and chlorine or bromine[42,43] indicates the existence of some types of complex in solution and that, under certain conditions, hydroxyhalides of selenium with an Se : Cl(Br) ratio of 1 : 2 may be formed.

Spectrophotometric examination of hydrochloric acid solutions containing Te^{IV} showed[44] that more than one type of ion exists in such a solution. At high HCl concentrations (9–12 *N*) two maxima, at 269 and 376 mμm, are observed in the absorption spectrum. In 6 *N* HCl the maximum at 269 mμm disappears and that at 376 mμm is noticeably reduced. Since halogeno-complexes of tellurium are coloured, solutions containing these compounds are used in the presence of hydrochloric acid, bromides, and iodides in photometric methods of determining tellurium[24,34-36,45-47].

The difference in the properties of compounds of selenium and tellurium present in hydrochloric acid solution and the possibility of the formation of several types of complex ion by these elements are used in extraction and ion-exchange methods of separating selenium and tellurium.

A study of the sorption of selenium and tellurium by ion exchangers in hydrochloric acid solution allowed Ermakov and coworkers[48] to perfect conditions for the quantitative separation of tellurium and selenium on EDE-10 anion--exchange resin†.

Tribenzylamine in chloroform was used as extractant in the separation of selenium and tellurium[49]. Using this solvent it was found possible to separate selenium and tellurium completely from 4–6 *N* HCl. Tellurium passes completely into the organic phase, while selenium remains in the aqueous solution. *N*-Dodecyltrialkylmethylamine in xylene has also been used as solvent.

The use of tributyl phosphate for the separation of selenium and tellurium, of telurium(IV) and tellurium(VI), and the removal of selenium and tellurium from iodine and sulphate ion has been described by Inarida[50-53]. It was established that tellurium(IV) is quantitatively extracted from 4–12 *N* HCl by 30% tributyl phosphate in kerosene, and a higher concentration of hydrochloric acid, about 6–12 *N* HCl, is required for selenium to pass into the organic phase. Thus the acidity must be made 4–5 *N* in HCl for the separation of selenium and tellurium. The use of 20% tributyl phosphate in kerosene as solvent allows Te^{VI} and Te^{IV} to be separated in hydrochloric acid solution (4–10 *N*). If 100% tributyl phosphate is used, the separation takes place over a still greater range of hydrochloric acid concentration, from 2 to 10 *N*.

† EDE-10P is a polyfunctional weakly or strongly basic anion--exchange resin prepared by the condensation of polyethylene-polyamines with epichlorohydrin, and contains secondary, tertiary, and quaternary nitrogen groups (Ed. of Translation).

Extraction with 100% tributyl phosphate from 0.2 *N* HCl is used to remove iodide ion[53]. Under these conditions the iodide passes quantitatively into the organic solvent phase. The acidity is then increased and tellurium(IV) is extracted from 4 *N* HCl.

Sulphate ion is removed in 4–12 *N* HCl with 30% tributyl phosphate in kerosene.

Selenium and tellurium are removed from other elements using isobutyl methyl ketone, 99% of the selenium and 96% of the tellurium being extracted from hydrochloric acid solution[54].

The use of a hydrochloric acid medium for the separation of selenium and tellurium by extraction is based on the difference in stability of their halogeno-complexes. An examination of separation methods described in the literature shows that Te^{IV} forms stable halogeno-complexes over a wider range of acidity than Se^{IV}, and the latter over a wider range than Te^{VI}. Extraction of selenium and tellurium with amines and tributyl phosphate under these conditions is probably connected with the formation of definite chemical compounds of the type solvent–acido-complex of Se or Te.

II. COMPLEXES OF SELENIUM AND TELLURIUM WITH LIGANDS CONTAINING NITROGEN

1. Compounds of Selenium and Tellurium with Organic Bases and Ammonia

The reaction of tellurium tetrachloride or tetrabromide dissolved in anhydrous ether, glacial acetic acid, benzene, alcohol, or acetone with aromatic amines gives the following compounds[55-60]:

$(C_6H_5NH_2)_2.TeBr_4$, $[(C_6H_5)_2NH]_2.TeBr_4$,
$(BrC_6H_4NH_2)_2.TeBr_4$, $(C_{10}H_7NH_2)_2.TeBr_4$,
$[C_6H_4(NH_2)_2].TeBr_4$, $[C_7H_6(NH_2)_2].TeBr_4$,
$[NH_2C_6H_4.C_6H_4NH_2].TeBr_4$, etc.

All these compounds crystallise well, are stable in air, but are decomposed by water; they are insoluble in ether, ethanol, chloroform, benzene, and carbon tetrachloride, but dissolve easily in acids. Some derivatives, for example the compounds with toluidine and *o*-phenylenediamine, are easily soluble in acetone. Tronev and coworkers[57] obtained the following compounds of $TeCl_4$ and $SeCl_4$ with ethylenediamine (En), pyridine (Py), aniline (An), thiourea (Thio), and ammonia:

$SeCl_4.4NH_3$, $SeCl_4.2Thio$, $SeCl_4.2En$,
$TeCl_4.2NH_3$, $TeCl_4.6NH_3$, $TeCl_4.2En$,
$.TeCl_4.2En.2NH_3$, $TeCl_4.2An$, $TeCl_4.2An.2NH_3$,
$TeCl_4.2Py$, $TeCl_4.2Thio$, $TeCl_4.6Thio$.

The thermal stability of these compounds was studied and it was shown that the bond between selenium or tellurium and the ligand containing nitrogen is characterised by a fairly high stability, especially in the case of ethylenediamine.

$TeBr_4$ forms compounds of the composition $(C_4H_4N_2).TeBr_4$ with diazines (pyrimidine, pyrazine, etc.). Similar 1 : 1 complexes were obtained with N_4S_4, $N_4S_4H_4$, and dioxan[26].

When heated in HBr solution the compounds with diazines $(C_4H_4N_2).TeBr_4$ are converted easily into crystalline salts $(C_4H_5N_2).TeBr_5$. The corresponding chlorides and iodides

can be obtained analogously. Aynsley[26] showed that for the diazine derivatives the stability of the TeX_5^- anion increases from the chloride to the iodide.

In the case of fluorides a white crystalline compound with pyridine $(C_5H_5N).TeF_4$ was obtained but $(C_5H_5N)_2.TeF_4$, which is expected by analogy with the chlorides and bromides, where the number of amine molecules combined with one $TeCl_4$ molecule is determined by the number of amino-groups in the molecule, was not obtained.

Tetrafluoropyridinetellurium(IV) $(C_5H_5N).TeF_4$ undergoes no change in air but is easily decomposed by water to form tellurous acid. In HF solution yellow crystalline pyridinium pentafluorotellurate(IV) $(C_5H_5NH)TeF_5$ is formed. This compound could not be converted into the corresponding chloro-, bromo-, or iodo-compound by using the appropriate hydrogen halide because in all cases the compounds $(C_5H_5NH)_2TeX_6$ were formed.

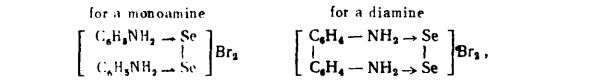
With urea, pentahalogenotellurates(IV) with the general formula $(CON_2H_5).TeX_5$, where X = Cl, Br, or I, were obtained[26].

Dipyridinium hexafluorotellurate(IV) $(C_5H_5NH)_2TeF_6$ is obtained in a solution of TeO_2 and pyridine in concentrated HF. When treated with HI it gave dipyridinium hexaiodotellurate(IV) $(C_5H_5NH)_2TeI_6$, and it is easily converted by the action of HCl and HBr, into $(C_5H_5NH)_2TeCl_6$ or $(C_5H_5NH)_2TeBr_6$. Dipyridinium hexaiodotellurate(IV) is formed on treating any other hexahalogenotellurate(IV) with hydriodic acid.

Many hexahalogenotellurates(IV) of amines (primary, secondary, and tertiary)[61-64], *N*-acetylamine[65], and alkaloids[66] are at present known and their properties have been studied. In some acetyl derivatives of hexahalogenotellurates(IV) three or four *N*-acetylamine molecules are combined with one H_2TeCl_6 molecule[65].

Whereas with tellurium the complexes with amines (and with some other organic bases) are numerous, for selenium only isolated examples are known. Tronev[57] obtained the compounds $SeCl_4.4NH_3$, $SeCl_4.2Thio$, and $SeCl_4.2En$. Compounds of amines with selenium oxide halides are also known: $2SeOCl_2.3(CH_3)_2NH.HCl$, $SeO_2.(CH_3)_2NH.HCl$, $2SeBr_4.SeBr.3(CH_3)_2NH.HBr$, $SeBr_4.2(CH_3)_2NH.HBr$, and some others[67].

The amino-derivatives of selenium monobromide[58,59]:



have been obtained with aniline, *o*-toluidine, *m*-toluidine, *o*-anisidine, benzylamine, α-naphthylamine, benzidine, and some other amines. These compounds are stable in air, insoluble in water and organic solvents, are hydrolysed by water on boiling, and are decomposed by dilute acids and alkalis.

There is little published information on the composition, structure, and properties of the ammines of selenium and tellurium. It is known from old work[31,68-70] that ammines, amides, imides, and nitrides of various compositions can be formed in the reaction of $SeCl_4$ and $TeCl_4$ with ammonia. SeO_2 reacts with liquid ammonia to give selenium nitride $(NSe)_x$.[71,72]

Tronev and coworkers[57] examined the series of compounds formed by the action of anhydrous ammonia on $TeCl_4$ and $SeCl_4$ at elevated pressure and temperature. $SeCl_4.4NH_3$, $TeCl_4.4NH_3$, and $TeCl_4.6NH_3$, and also compounds of a mixed type $TeCl_4.2En.2NH_3$ and $TeCl_4.2An.2NH_3$ were obtained by this method.

Ammines were converted into amides and ammonium chloride by repeated washing with liquid ammonia.

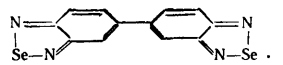
Amino-compounds of selenium, obtained from the reaction of elementary selenium with ammonia and oxygen under pressure at 50–100°, have also been studied.

The reaction of selenium dioxide difluoride with ammonia[74] gives a mixture of the ammonium salts of cyclic triselenimide $(SeO_2NNH_4)_3$ and a homologous series of cyclic polyimidoamides of selenous acid $NH_2SeO_2N(NH_4)_nSeO_2NH_2$.[74]

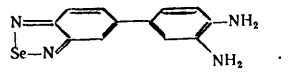
Dostal[75] obtained and investigated the amidoselenates of silver, $Ag(SeO_3NH)$, and of alkali and alkaline earth metals.

2. Compounds of Selenium with 3,3′-Diaminobenzidine and Some Other *o*-Diamines

Selenous acid reacts in hydrochloric acid solution with 3,3′-diaminobenzidine to form a yellow crystalline precipitate which is insoluble in both acidic and alkaline media. Dipiazoselenol, m.p. 292–314°, is formed in solutions containing an excess of selenous acid[2,76,77]

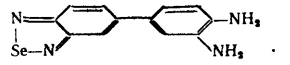


Monopiazoselenol, dark red crystals with m.p. 202°, can be formed when there is insufficient selenium[77].



Tellurium does not react with diaminobenzidine.

A highly sensitive and specific method for determining selenium is based on the ability of the latter to form a yellow coloration with diaminobenzidine in dilute solutions, Monopiazoselenol — 3,4-diaminophenylpiazoselenol — being formed in solution[77]:



Hinsberg[78] first discovered the ability of diamines (naphthylenediamines) to react with selenium and so form coloured solutions.

The method of determining selenium with 3,3′-diaminobenzidine was proposed by Hoste and Gillis[2,76]. Piazoselenol is formed quantitatively in acid medium. As the acidity is increased the intensity of the colour increases but the rate of the reaction falls. The colour of the compound of selenium with 3,3′-diaminobenzidine is stable in 0.1 *N* HCl. The maximum of the absorption spectrum is at 350 mμm and the molar extinction coefficient is 10200.

Further research showed that the sensitivity and specificity of the reaction are increased by extracting the coloured selenium compound with organic solvents — toluene, benzene, chloroform, isopentanol, pentyl acetate, etc.[79]

A pH of 2–3 provides the best conditions for formation of Piazoselenol, the reaction rate being greater in formic acid than in hydrochloric acid. The coloured compound

is extracted with the organic solvents at pH 6–7. There are maxima in the absorption spectrum of the coloured compound in toluene at 340 and 420 mμm, but the reagent absorbs strongly at 340 mμm and therefore the measurement of optical density is usually made at 420 mμm. The molar extinction coefficient at this wavelength is 19 900.

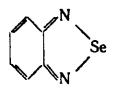
The colour of solutions containing Piazoselenol depends markedly on temperature and is somewhat weakened by the action of light. It is therefore recommended to heat the solutions of Piazoselenol on a water-bath before extraction and to protect the solutions from sunlight after the reaction has been completed[80].

Solutions in toluene which contain Piazoselenol fluoresce in the region of 420 and 580 mμm. The sensitivity of the reaction can be increased considerably by determining the selenium fluorimetrically[77,81,82].

In recent years there have been many published papers on the use of the reaction of selenium with diaminobenzidine — the determination of selenium in sulphur and sulphuric acid[83-88], in tellurium metal[98], in copper, lead, and other metals[90-93], in steels[91,93], and in organic substances and biological materials[91,92,94-97].

Examination of other aromatic *o*-diamines showed that *o*-phenylenediamine is also suitable for the determination of small quantities of selenium[98], the sensitivity of this reaction being somewhat higher than of that with 3,3′-diaminobenzidine[99].

An X-ray structural investigation of the compound of selenium and *o*-phenylenediamine showed that its structure can be represented[100]:



Other diamines also form coloured compounds with selenium, *e.g.* 1,8-naphthylenediamine[101], 4-dimethylamino--1,2-phenylenediamine, and 4-methylthio-1,2-phenylenediamine[91,102].

3. Compounds of Tellurium with Thiourea and Its Derivatives

A compound of tellurium with thiourea was first prepared[103] in 1927, as a yellow crystalline substance with m.p. 165° which is very soluble in alcohol, ether, and other organic solvents.

The reaction of TeX_4, where X = Cl or Br, with thiourea in alcoholic solution gives several compounds[104]: $(SCN_2H_4)_2.TeCl_4$ (m.p. 175°), $(SCN_2H_4)TeBrO_4$ (m.p. 210°), $(SCN_2H_3)_2.TeCl_2$, $(SCN_2H_3)_2TeBr_2$ (m.p. 215°), $(SCN_2H_5)_2.TeCl_6$, $(SCN_2H_5)_2.TeBr_6$ (m.p. 155°), $(SCN_2H_5)_2.TeI_6$, $(SCN_2H_5)_2.TeCl_6.2SCN_2H_5Cl$ (m.p. 155°), and $(SCN_2H_5)_2.TeBr_6.2SCN_2H_5Br$ (m.p. 155°).

Tronev and coworkers[57] obtained several compounds of selenium and tellurium with thiourea: $SeCl_4.2SCN_2H_4$, $TeCl_4.2SCN_2H_4$, and $TeCl_4.6SCN_2H_4$.

Vřeštal[105] isolated a number of thiourea compounds of tellurium from aqueous solutions and showed that all the complexes are derivatives of tellurium(II) because in acid aqueous solution thiourea reduces Te^{IV} to Te^{II}. In solutions of various inorganic acids tellurium(II) forms the following yellow crystalline compounds, which are sparingly soluble in water, with thiourea: $Te(SCN_2H_4)_4Cl_2.2H_2O$ (m.p. 175°), $Te(SCN_2H_4)_2Cl_2$ (m.p. 184°), $Te(SCN_2H_4)_2Br_2$ (two modifications with m.p. 170° and 220°), $Te(SCN_2H_4)_4(ClO_4)_2$ (m.p. 144°), $Te(SCN_2H_4)_4(NO_3)_2.2H_2O$ (m.p. 117°), $Te(SCN_2H_4)_4.SO_4.2H_2O$ (m.p. 141°), and $Te(SCN_2H_4)_4(HC_2O_4)_2.2H_2O$ (m.p. 170°). These compounds are readily soluble in polar solvents but insoluble in non-polar solvents.

In 1959–1961 papers by Foss and coworkers[5-17] described the preparation and some of the properties of complexes of tellurium with thiourea and its derivatives (ethylenethiourea, propylenethiourea, and tetramethylthiourea).

Six-coordinated complexes of tellurium(IV) and tetramethylthiourea (Tmthio) have been obtained: $Te(Tmthio)_2.Cl_4$ (m.p. 153–154°) and $Te(Tmthio)_2Br_4$ (m.p. 176–177°). The dark red crystals of these compounds became dull in the air and they were very rapidly decomposed by water to white H_2TeO_3. When dissolved in an acidic (4 *N* HCl) aqueous methanol solution these substances were rapidly converted into compounds of tellurium(II).

The tetrachloro- and tetrabromo-compounds of tellurium and tetramethylthiourea are the only representatives of compounds of tellurium(IV). All other compounds with thiourea are derivatives of tellurium(II).

The reduction of tellurium(IV) to tellurium(II) by thiourea can be represented by the equation

$$Te^{IV}+4SCN_2H_4+2X^-\rightarrow Te^{II}(SCN_2H_4)_2X_2+[(NH_2)_2CSSC(NH_2)_2]^{2+};$$

the thiourea is oxidised to formalin disulphide.

In an aqueous methanol solution containing Te^{IV} and HCl (or HBr), tetramethylthiourea forms the compounds $Te(Tmthio)Cl_2$ (m.p. 207°) and $Te(Tmthio)Br_2$ (m.p. 226°). The dark red crystals of these compounds are isomorphous and are triclinic.

Four-coordinated complexes with general formula TeR_2X_2, where X = Cl, Br, I, or SCN and R = Thio, Tmthio, Ethio (ethylenethiourea), or Prthio (propylenethiourea), have been obtained.

Thiourea gives $Te(Thio)_2Cl_2$ (m.p. 220°), $Te(Thio)_2Br_2$ (m.p. 220°), $Te(Thio)_2I_2$, and $Te(Thio)_2(SCN)_2$. The crystals of these four complexes are isomorphous and they are *cis*-isomers.

From ethylenethiourea two modifications of the bromide $Te(Ethio)_2Br_2$ were isolated, yellowish brown orthorhombic prisms with m.p. 186° (*cis*-isomer) and reddish yellow monoclinic prisms with m.p. 192° (*trans*-isomer). Both compounds are insoluble in methanol and glacial acetic acid, but readily soluble in dimethylformamide.

$Te(Ethio)_2I_2$, red monoclinic crystals with m.p. 198–200° which are isomorphous with the *trans*-bromide, and $Te(Ethio)_2(SCN)_2$, yellow prisms with m.p. 142–144°, were also obtained.

A chloride, bromide, thiocyanate, and methanethiosulphonate, of which the first two are *cis*-isomers and the last two *trans*-isomers, were prepared from propylenethiourea: $Te(Prthio)_2Cl_2$ (m.p. 199°), $Te(Prthio)_2Br_2$ (m.p. 190°), $Te(Prthio)_2(SCN)_2$ (m.p. 214°), and $Te(Prthio)_2.(S_2O_2CH_3)_2$ (m.p. 172°).

From tetramethylthiourea were obtained the *trans*-isomers $Te(Tmthio)_2Cl_2$ (m.p. 167°) and $Te(Tmthio)_2Br_2$ (m.p. 192°) as reddish orange crystals and two crystalline modifications of *cis*- and *trans*-$Te(Tmthio)_2I_2$.

On forming compounds of the type $Te(Thio)_2X_2$ it is possible to replace the chloride or bromide ions by methanethiosulphonate or benzenethiosulphonate. The following have been isolated: $Te(Thio)_2(S_2O_2CH_3)_2$ (m.p. 130–131°), $Te(Ethio)_2(S_2O_2CH_3)_2$ (two isomers, *cis*- and *trans*- with m.p. 168°), $Te(Ethio)_2(S_2O_2C_6H_5)_2$, $Te(Tmthio)_2(S_2O_2CH_3)_2$, and $Te(Tmthio)_2(S_2O_2C_6H_5)_2$.

No fluoride of the type $Te(Thio)_2X_2$ was obtained.

Foss and coworkers also obtained compounds with three molecules of thiourea (or ethylenethiourea, or propylenethiourea): $Te(Thio)_3(HF_2)_2$, $Te(Ethio)_3(ClO_4)_2$, and $Te(Prthio)_3(ClO_4)_2$. Two modifications of the yellowish green crystals of the last compound, monoclinic and triclinic, were isolated.

Finally, the following complexes with four molecules of thiourea (or its derivatives) were obtained: $Te(Thio)_4Cl_2.2H_2O$, $Te(Thio)_4Cl_2$, $Te(Thio)_4Br_2$, $Te(Thio)_4(SCN)_2$, $Te(Thio)_4(NO_3)_2$, $Te(Thio)_4(ClO_4)_2$, $Te(Thio)_4(HF_2)_2$, $Te(Thio)_4F_2.2H_2O$, $Te(Ethio)_4Cl_2.2H_2O$, $Te(Ethio)_4Br_2.2H_2O$, $Te(Ethio)_4Cl_2$, $Te(Ethio)_4Br_2$, $Te(Ethio)_4(ClO_4)_2$, $[Te(Ethio)_4][TeCl_6]$, $Te(Prthio)_4Cl_2.2H_2O$, and $Te(Prthio)_4.(ClO_4)_2$. Acidic aqueous and ethanol solutions of these compounds saturated with thiourea are stable.

The ethylenethiourea dihydrates are readily soluble in acidic aqueous and methanol solutions, and also in dimethylformamide to form orange solutions which are stable at room temperature. Boiling methanol dissolves about 1.5 g of the substances per 100 ml; anhydrous salts crystallise from such solutions on cooling.

Thiourea, ethylenethiourea, and propylenethiourea form a cationic complex of type $Te(Thio)_4^{2+}$, but not tetramethylthiourea. Steric hindrance probably occurs for the last compound. It was, however, possible to isolate compounds containing two molecules of thiourea and two of tetramethylthiourea: $[Te(Thio)_2(Tmthio)_2]Cl_2$ and $[Te(Thio)_2(Tmthio)_2]Br_2$.

The formation of the coloured $[Te(Thio)_4]^{2+}$ complex in solutions saturated with thiourea is used for the quantitative determination of small amounts of tellurium. Selenium is reduced by thiourea to the element and does not interfere with this determination.

Jilek and Vřeštal[106–110] developed a photometric method for determining tellurium(IV) in the presence of tellurium(VI). They established that the rate of the reaction of Te^{IV} with thiourea depends on the solution pH, concentration of thiourea, and temperature. The maximum coloration is observed in perchloric acid medium (0.8 *N* $HClO_4$) in a solution saturated with respect to thiourea.

Nielsch[111–113] developed a method for determining tellurium by the reaction with thiourea in nitric acid (5–10% HNO_3), phosphoric acid (2–10% H_3PO_4), or sulphuric acid (2–6% H_2SO_4) solutions with a 10–11% thiourea concentration. A maximum was observed in the absorption spectrum at 310–320 mμm. The high sensitivity (1 mg Te in 1 ml) and specificity of the reaction permits the determination of tellurium in copper and selenium, which is especially important for the production of pure selenium.

The determination of tellurium in cast ion by means of the reaction with thiourea is carried out in nitric acid (6% HNO_3).[114]

Leontovitch[115] determined tellurium in ferruginous products using a phosphoric acid medium. Gladyshev[116] used thiourea for the colorimetric determination of tellurium in dusts from lead manufacture.

In the presence of potassium thiocyanate a compound of tellurium and thiourea is extracted from hydrochloric acid solution (0.6–1.7 *N* HCl) by tributyl phosphate[117]. Using an excess of KSCN it is possible to determine very small quantities of tellurium.

III. COMPLEXES OF SELENIUM AND TELLURIUM WITH LIGANDS CONTAINING SULPHUR

1. Complexes of Selenium and Tellurium with Thiosulphate and Its Derivatives

In acidic solutions selenium(IV) and tellurium(IV) are reduced by sodium thiosulphate to selenium(II) and tellurium(II), forming yellow solutions containing the complex ions $[Se(S_2O_3)_2]^{2-}$ or $[Te(S_2O_3)_2]^{2-}$ which are called seleno- or telluro-pentathionate by analogy with pentathionate $[S(S_2O_3)_2]^{2-}$. Selenium and tellurium replace the middle sulphur atom in the pentathionate, forming an unbranched chain –S–S–Te–S–S–.

The pentathionate is formed by the reaction:

$$SeO_2+4Na_2S_2O_3+4HCl=Na_2[Se(S_2O_3)_2]+Na_2S_4O_6+4NaCl+2H_2O.$$

A study of the properties of solutions containing compounds of selenium and tellurium with thiosulphate showed that they are easily decomposed by alkali solutions with separation of elemental selenium and tellurium, but that they are perfectly stable towards acids. Dilute solutions of the compounds can be boiled for some time in the presence of an excess of thiosulphate without fear of decomposition but they decompose slowly in water.

Salts of seleno- and telluro-pentathionic acids were first isolated by Foss[118–120], who obtained the following: $Na_2[Se(S_2O_3)_2].3H_2O$, $Na_2[Te(S_2O_3)_2].2H_2O$, $K_2[Se(S_2O_3)_2].1.5H_2O$, $K_2[Te(S_2O_3)_2]$, $(NH_4)_2[Se(S_2O_3)_2].1.5H_2O$, $(NH_4)_2.[Te(S_2O_3)_2]$, $Rb_2[Se(S_2O_3)_2].1.5H_2O$, $Rb_2[Te(S_2O_3)_2].1.5H_2O$, $Cs_2[Se(S_2O_3)_2]$, and $Cs_2[Te(S_2O_3)_2].1.5H_2O$.

The compounds were isolated as well-formed crystals, the hydrates usually forming more regular crystals. All the compounds are yellow or yellowish green; as a rule, the hydrates are more strongly coloured than the anhydrous compounds. The water molecules in the hydrates are not removed by keeping the substances in a vacuum over sulphuric acid.

The salts which are isolated pure are quite stable and can be kept for some weeks without decomposing. Their solubility in water decreases in the order Na > NH_4 > K > Rb > Cs, the tellurium salts being somewhat less soluble in water than those of selenium. The Na and NH_4 salts are usually appreciably soluble in methanol and somewhat in 96% ethanol, whereas the K, Rb, and Cs salts are insoluble in alcohols.

Selenopentathionate and telluropentathionate react rapidly and quantitatively with diethyldithiocarbamate to form the compounds $Se[S_2CN(C_2H_5)_2]_2$ and $Te[S_2CN(C_2H_5)_2]_2$.

Examination of the crystal structure of ammonium telluropentathionate $(NH_4)_2[Te(S_2O_3)_2]$ showed[121] that the $[Te(S_2O_3)_2]^{2-}$ ion contains an unbranched –S–S–Te–S–S– chain which has a *trans*-configuration, and the three oxygen atoms are arranged in tetrahedral positions. Hydrogen links

the oxygen atoms and the nitrogen atoms of the ammonium ions.

The thiosulphate complexes of sulphur(II), selenium(II), and tellurium(II) form isomorphous crystals.

Foss synthesised a new type of compound — derivatives of methanethiosulphonate [122,123], $Se(S_2O_2CH_3)_2$ and $Te(S_2O_2CH_3)_2$. These compounds are analogous to the pentathionates, the hydroxy-group of the acid being replaced by methyl.

Telluro- and seleno-bismethanethiosulphonates were obtained as greenish yellow crystals which are insoluble in water, moderately soluble in cold chloroform and ethyl acetate, and insoluble in ether, carbon disulphide, and benzene. The compounds are fairly stable in air and do not change over a period of months. They are decomposed by alkali with separation of elemental sulphur, selenium, and tellurium. Other thiosulphonate derivatives of selenium and tellurium — the bisbenzenethiosulphonate $Te(S_2O_2C_6H_5)_2$ [124,126] and *p*-toluenethiosulphonates [127] — were also obtained. The compounds containing benzene are more stable than those containing *p*-toluene. $Se(S_2O_2C_6H_5)_2$ is fairly readily, and $Te(S_2O_2C_7H_7)_2$ moderately, soluble in warm ethyl acetate, benzene, and chloroform [124].

In these compounds tellurium(II) easily liberates the R-thiosulphonate group in substitution reactions with thiosulphate and diethyldithiocarbamate and forms telluropentathionate and tellurodiethyldithiocarbamate.

Another compound which forms crystals isomorphous with selenium and tellurium sulphonates was obtained; this is the triselenium disulphinate $Se_3(SO_2R)_2$, in which three sulphur atoms have been replaced by three selenium atoms.

Foss [128] also obtained selenium disulphinate $Se(SO_2R)_2$ and diselenium disulphinate $Se_2(SO_2R)_2$, from diselenium dichloride by reaction with an excess of sodium benzenesulphinate and *p*-toluenesulphinate suspended in benzene and ether.

The course of the reaction depends on the nature of the solvent. In benzene mainly diselenium disulphinate is formed,

$$Se_2Cl_2+2RSO_2Na=Se_2(SO_2R)_2+2NaCl,$$

whereas in ether selenium and triselenium disulphinates are produced,

$$2Se_2Cl_2+4RSO_2Na=Se(SO_2R)_2+Se_3(SO_2R)_2+4NaCl.$$

In chloroform containing no ethanol equal amounts of diselenium and triselenium disulphinate are formed.

Crystals of $Se(SO_2C_6H_5)_2$ and $Se(SO_2C_7H_7)_2$ are stable in air, rapidly liberate selenium in sunlight, decompose on heating, are insoluble in water, slightly soluble in warm ligroin, moderately soluble in warm ether, ethanol, and acetic acid, and readily soluble in chloroform, warm benzene, and carbon tetrachloride. Ether solutions of $Se_2(SO_2C_7H_7)_2$ are stable on heating. Solutions of diselenium and triselenium disulphinates in chloroform and ethanol are completely hydrolysed by aqueous alkali. Selenium sulphinates form greenish yellow crystals, the green colour becoming deeper as the number of selenium atoms increases.

Two moles of thiourea can be added to tellurium thiosulphonate to form the mixed compounds $Te(Thio)_2(S_2O_2CH_3)_2$, $Te(Ethio)_2(S_2O_2CH_3)_2$, $Te(Ethio)_2(S_2O_2C_6H_5)_2$, $Te(Tmthio)_2.(S_2O_2CH_3)_2$, and $Te(Tmthio)_2(S_2O_2C_6H_5)_2$. All the compounds isolated are greenish yellow crystals except $Te(Tmthio)_2.(S_2O_2C_6H_5)_2$, which is red. They are completely stable as solids but decompose rapidly in water with liberation of elemental tellurium.

The ability of selenium and tellurium to form thiosulphate complexes is used in a number of titration methods for determining these elements [24,129].

2. Compounds of Selenium and Tellurium with Diethyldithiocarbamate and Its Derivatives

With diethyldithiocarbamate (DDTC) tellurium forms a coloured compound $Te(DDTC)_4$ which is insoluble in water and on extraction passes easily into the layer of organic solvent — chloroform, carbon tetrachloride, etc.[130] Selenium forms a similar compound.

The selenium complex passes quantitatively into the organic phase at pH 4–6.2 but tellurium is extracted over a wider pH range, 4–8.8. The separation of selenium and tellurium carbamates by extraction is usually carried out at pH 8.5–8.7.[131] The presence of complexones in solution, and also of cyanides, citrates, tartrates, phosphates, and borates does not affect the extraction of selenium and tellurium.

The measurement of the optical density of tellurium diethyldithiocarbamate solutions in chloroform is made at 428 mμm,[132–134] the molar extinction coefficient being 3200. Aqueous acetone solutions containing the tellurium compound have an absorption maximum at 340 mμm.[135]

Solutions containing tellurium diethyldithiocarbamate are unstable and are rapidly decolorised, especially in light. Photometry of the solutions must therefore be carried out immediately after development of the colour, using a vessel made of dark glass.

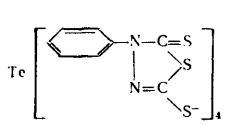
Determination of tellurium with diethyldithiocarbamate is used in the analysis of iron and steels [136], pure selenium [137], platinum metals [138], and lead and copper [92].

Sodium 3,5-diphenylpyrazoline-1-dithiocarbamate forms a yellow compound with tellurium, which is readily soluble in chloroform and carbon tetrachloride and is more stable than tellurium diethyldithiocarbamate in solutions in organic solvents.

The compound of tellurium with 3,5-diphenylpyrazoline-1-dithiocarbamate is extracted by chloroform over a wide acidity range — from 12 *N* HCl to pH 9. The absorption spectrum of solutions in chloroform has a maximum at 415 mμm and the apparent molar extinction coefficient is 20 400 at this wavelength [139].

3. Compounds of Tellurium with Bismuthol-II (Mercaptophenylthiolthiadiazolone)

With tellurium, Bismuthol-II forms a coloured compound



which is insoluble in water but passes easily into an organic phase; at pH 5–8 it is extracted by alcohols, ketones, chloroform, and carbon tetrachloride. The extraction reaches a maximum at pH 3.3–4.3.[3]

Quantitative formation of the compound in aqueous solution is observed at pH 2.0–2.2.[4] At pH 8 the compound decomposes. A complex of selenium with Bismuthol-II is formed at a higher acidity.

The colour of solutions of the tellurium compound in organic solvents is stable on standing and has an absorption maximum at 335 mμm, but quantitative measurements are made at 415 mμm, where the absorption of the reagent is minimal. At this wavelength the molar extinction coefficient is 28 000.

Bismuthol-II is used to determine traces of tellurium in ores and in pyrites[3] and to determine tellurium in cadmium and mercury tellurides[140].

IV. OTHER COMPLEXES OF SELENIUM AND TELLURIUM

Nickel diethyldithiophosphate reacts[141,142] with selenous acid to form a yellowish amorphous precipitate of $[(C_2H_5O)_2PSS]_2Se$. Selenium(II) diethyldithiophosphate is quite stable, is insoluble in water, but dissolves readily in organic solvents (chloroform, carbon tetrachloride, benzene, etc.) forming coloured solutions with an absorption maximum at 315–320 mμm. However, the disulphide absorbs considerably in this region, so that this reaction cannot be used for the quantitative determination of selenium.

When a solution of $TeCl_4$ in benzene reacts with dicarboxylic acids[143] the following compounds are formed: $[(CH_2)_2(COO)_2]_2Te$ with succinic acid, $[(CH_2)_4(COO)_2]_2Te$ with adipic acid, and $[C_6H_4(COO)_2]_2Te$ with phthalic acid.

Hydroxy-acids (salicylic, gallic, tannic, malonic) form the following compounds with tellurium:

$$(HOC_6H_4COO)_4Te, \quad [(HO)_3C_6H_2COO]_4Te,$$
$$(C_{14}H_8O_9)_2Te, \quad [CH_2.CHOH.(COO)_2]_2Te.$$

All the substances isolated are soluble in ethanol, acetone, and ethylacetone [ethyl acetate? (Ed. of Translation)], but insoluble in ether, chloroform, and carbon tetrachloride.

Tellurium forms heteropolyacids in which tellurium(IV) or tellurium(VI) can be the central atom. Rosenheim and Traube[144] obtained heteropoly compounds of tellurium(VI) of the type $R_6[Te(WO_3)_6]$, where R = Na, K, NH_4, or guanidinium.

Ganelina[145] synthesised the tetrabasic dodecatungstotelluric acid $H_4[TeO_4(H_2WO_4)_{12}].13H_2O$, which is a yellow crystalline powder, readily soluble in water. Aqueous solutions of the heteropolyacid are not decomposed by concentrated sulphuric acid. In hydrochloric acid solution the heteropolyanion $[TeO_4(H_2WO_4)_{12}]^{4-}$ is stable at an HCl concentration less than 1.138 *N*.

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Vernadskii Institute of Geochemistry
and Analytical Chemistry,
Academy of Sciences of the USSR