

presence of lithium perchlorate, while water slowly deposited elemental tellurium.

Kinetic study. The rate constants were determined by measuring the disappearance of the peaks at 2081 cm^{-1} (TeCN^-), 2068 cm^{-1} (SeCN^-), and 2059 cm^{-1} (SCN^-) at varying concentration of the pseudohalide ions and benzyl bromide in the $4-10 \times 10^{-3}$ M concentration range. The rate constants in Table I refer to measurements with initial concentrations of reactants of 6×10^{-3} M. When the thiocyanate ion and the selenocyanate were the nucleophiles, 0.1 cm liquid cells were used. Due to the considerably lower extinction coefficient of the tellurocyanate ion at 2081 cm^{-1} ,¹ 0.15 cm liquid cells were used in these reactions. The rate constants for the selenocyanate ion and the thiocyanate ion are probably good to $\pm 3\%$ while the rate constant for the reaction between the tellurocyanate ion and benzyl bromide is probably of considerably lower accuracy, $\approx \pm 5\%$, due to the high rate of this reaction. A very weak peak at ~ 2162 cm^{-1} could be observed in completed reaction mixtures. For all examined reactions, the rate plots were linear up to two or three half-lives. Due to traces of oxygen in the applied solvent, the rate constant for the very slow reaction between tetraphenylarsonium tellurocyanate and benzyl chloride could not be accurately determined.

The stoichiometry of the reaction between tetraphenylarsonium tellurocyanate and benzyl bromide was determined in more concentrated solutions by measuring the reduction of the peak due to the tellurocyanate ion as a function of added benzyl bromide. All measurements confirmed the reaction to be a 1:1 reaction.

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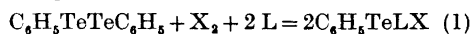
Reactions of Diphenylditelluride with Halogens in Presence of Ligands Containing Sulphur or Selenium as Donor Atoms

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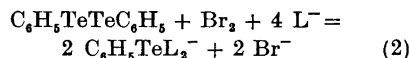
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Phenyltellurium trichloride dissolved in methanol reacts with aqueous thiourea (tu) to give thiourea complexes of divalent tellurium, $\text{C}_6\text{H}_5\text{Te}(\text{tu})\text{Cl}$ and $\text{C}_6\text{H}_5\text{Te}(\text{tu})_2\text{Cl}$.¹

It has now been found that diphenylditelluride dissolved in methanol reacts with halogen (chlorine or bromine) and ligands containing sulphur or selenium to form complexes of divalent tellurium:

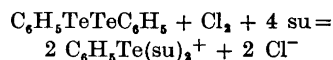


or



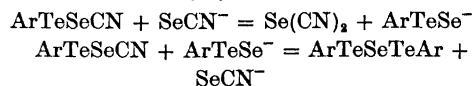
In the first case L is thiourea, selenourea, triphenylphosphineselenide, or trimorpholylphosphineselenide. In the second case L^- is thiocyanate or selenocyanate. The anionic complexes formed have been isolated as tetramethylammonium salts.

By use of 4 mol of selenourea (su) and 1 mol chlorine the complex $\text{C}_6\text{H}_5\text{Te}(\text{su})_2\text{Cl}$ was formed:



The analogous complex with thiourea is known.¹

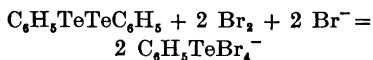
When potassium selenocyanate instead of tetramethylammonium selenocyanate was used in reaction (2) a blue-violet compound separated from the solution. The compound was shown to be bis(benzenetellurenyl) selenide, $\text{C}_6\text{H}_5\text{TeSeTeC}_6\text{H}_5$. A possible mechanism may be that benzenetellurenyl selenocyanate is formed first, and then ($\text{Ar} = \text{C}_6\text{H}_5$):



The same compound, bis(benzenetellurenyl) selenide, was isolated from a reaction between selenourea-benzenetellurenyl chloride, $\text{C}_6\text{H}_5\text{Te}(\text{su})\text{Cl}$, and potassium selenocyanate. The reaction is probably

similar to the conversion of the adduct of thiourea with *o*-nitrobenzeneselenenyl ion, $\text{ArSeSC}(\text{NH}_2)_2^+$, to bis(*o*-nitrobenzeneselenenyl)sulphide, ArSeSSeAr .²

In an attempt to prepare a phenyldibromotellurate(II) complex a compound which was shown to be tetramethylammonium phenyltetrabromotellurate(IV) crystallized from the solution:



There is probably, in the solution, an equilibrium between tellurate(II) and tellurate(IV). The solubility and the stability of the complexes under the conditions employed, favour the tellurate(IV).

Space groups and unit cell dimensions were determined from single-crystal oscillation and Weissenberg photographs using $\text{CuK}\alpha$ radiation. The unit cell dimensions are believed to be accurate to within 0.5%. Densities were determined by flotation. Melting points are corrected.

Diphenylditelluride was prepared according to the method of Haller and Irgolic.³ Potassium selenocyanate was prepared as described in *Inorganic Syntheses*.⁴ Tetramethylammonium selenocyanate was prepared as described elsewhere.⁵ Triphenylphosphineselenide and trimorpholyphosphineselenide were gifts from J. Songstad of this Institute.

Thiourea-benzenetellurenyl bromide, $\text{C}_6\text{H}_5\text{Te}(\text{tu})\text{Br}$. 2.5 mmol (1.025 g) of diphenylditelluride and 5 mmol (0.38 g) of thiourea were dissolved in 20 ml of warm methanol, and 2.5 mmol of bromine dissolved in 2.5 ml methanol was added under rapid stirring. After filtering, a clear orange red solution resulted, from which the compound crystallized on standing. Yield, 1.62 g (90%). The product was recrystallized from methanol, and identified by its melting point and by X-ray photographs. The thiourea-benzenetellurenyl bromide has earlier been prepared from phenyltellurium trichloride, thiourea, and potassium bromide.¹

Selenourea-benzenetellurenyl chloride, $\text{C}_6\text{H}_5\text{Te}(\text{su})\text{Cl}$, was prepared in the same way as the thiourea compound, using 2.5 mmol (1.025 g) of diphenylditelluride and 5 mmol (0.62 g) of selenourea, dissolved in 20 ml of warm methanol, and 2.5 mmol of chlorine dissolved in 5 ml methanol. Yield, 1.63 g (89%). It could be recrystallized from methanol (1 g dissolved in about 30 ml at boiling temperature). M.p. 165° (dec.). (Found: C 23.11; H 3.55; N 7.79. Calc. for $\text{C}_7\text{H}_9\text{ClN}_2\text{SeTe}$: C 23.14; H 3.42; N 7.71).

The crystals are orange-red, monoclinic prisms extended along the *a* axis, with $a = 6.28 \text{ \AA}$, $b = 10.70 \text{ \AA}$, $c = 15.34 \text{ \AA}$, $\beta = 90.6^\circ$. There are four molecules per unit cell; density, calc. 2.34, found 2.35 g/cm^3 . The space group, from systematic absences, is $P2_1/n$ (No. 14). The crystals are isomorphous with the corresponding thiourea complex.¹

Selenourea-benzenetellurenyl bromide, $\text{C}_6\text{H}_5\text{Te}(\text{su})\text{Br}$, was prepared and recrystallized as described above for the chloride, using 2.5 mmol (1.025 g) of diphenylditelluride and 5 mmol (0.62 g) of selenourea dissolved in 20 ml of warm methanol, and 2.5 mmol of bromine dissolved in 2.5 ml methanol. Yield, 1.46 g (72%). M.p. 195° (dec.). (Found: C 20.76; H 2.31; N 7.02. Calc. for $\text{C}_7\text{H}_9\text{BrN}_2\text{SeTe}$: C 20.62; H 2.21; N 6.87).

The crystals are isomorphous with those of the chloride, and have the same colour and morphology. The unit cell dimensions are, $a = 6.50 \text{ \AA}$, $b = 10.73 \text{ \AA}$, $c = 15.41 \text{ \AA}$, $\beta = 91.2^\circ$, density, calc. 2.52, found 2.51 g/cm^3 .

Trimorpholyphosphineselenide-benzenetellurenyl chloride, $\text{C}_6\text{H}_5\text{TeSeP}(\text{NC}_4\text{H}_9\text{O})_3\text{Cl}$, was prepared as described above for the selenourea compounds, using 1.25 mmol (0.50 g) of diphenylditelluride and 2.5 mmol (0.92 g) of trimorpholyphosphineselenide dissolved in 40 ml warm methanol, and 1.25 mmol of chlorine dissolved in 3.6 ml methanol. The compound was not recrystallized. Yield, 1.10 g (72%). M.p., 137° (dec.). (Found: C 35.47; H 4.72; N 6.87; O 7.89; P 5.02. Calc. for $\text{C}_{18}\text{H}_{29}\text{N}_3\text{O}_3\text{PClSeTe}$: C 35.53; H 4.77; N 6.91; O 7.89; P 5.09).

The crystals form orange-red, monoclinic prisms extended along the *a* axis, with $a = 9.13 \text{ \AA}$, $b = 18.70 \text{ \AA}$, $c = 14.76 \text{ \AA}$, $\beta = 116.4^\circ$. There are four molecules per unit cell; density, calc. 1.78, found 1.77 g/cm^3 . The space group, from systematic absences, is $P2_1/c$ (No. 14).

Trimorpholyphosphineselenide-benzenetellurenyl bromide, $\text{C}_6\text{H}_5\text{TeSeP}(\text{NC}_4\text{H}_9\text{O})_3\text{Br}$, was prepared as described above for the chloride, using 1.25 mmol bromine dissolved in 2.4 ml methanol instead of the chlorine solution. Yield, 1.30 g (79%). M.p., 138° (dec.). (Found: C 33.03; H 4.35; N 6.35; O 7.32; P 4.87. Calc. for $\text{C}_{18}\text{H}_{29}\text{N}_3\text{O}_3\text{PBrSeTe}$: C 33.11; H 4.44; N 6.44; O 7.36; P 4.75).

The crystals are isomorphous with those of the chloride, and show the same colour and morphology. The unit cell dimensions are, $a = 9.23 \text{ \AA}$, $b = 18.84 \text{ \AA}$, $c = 14.86 \text{ \AA}$, $\beta = 117.2^\circ$. Density, calc. 1.88, found 1.87 g/cm^3 .

Triphenylphosphineselenide-benzenetellurenyl bromide, $\text{C}_6\text{H}_5\text{TeSeP}(\text{C}_6\text{H}_5)_3\text{Br}$, was prepared in the same way as trimorpholyphosphineselenide-benzenetellurenyl bromide, using 1.25

mmol (0.50 g) of diphenylditelluride and 2.5 mmol (0.86 g) of triphenylphosphineselenide dissolved in 40 ml of methanol, and 1.25 mmol of bromine dissolved in 2.5 ml methanol. Yield, 1.1 g (70 %). M.p., 127° (dec.). (Found: C 46.14; H 3.30; P 4.96. Calc. for $C_{24}H_{20}PBrSeTe$: C 46.05; H 3.20; P 4.95).

The crystals are orange-red, monoclinic prisms extended along the long *ac* diagonal, with $a=12.79$ Å, $b=9.93$ Å, $c=18.60$ Å, $\beta=104.8^\circ$. There are four formula units per unit cell; density, calc. 1.82, found 1.80 g/cm³. The space group, from systematic absences, is $P2_1/n$ (No. 14).

Diselenourea-benzenetellurenyl chloride, $C_6H_5Te(su)_2Cl$. To a solution of 2.5 mmol (1.025 g) of diphenylditelluride and 10 mmol (1.23 g) of selenourea in 30 ml of warm methanol was added slowly under vigorous stirring, 2.5 mmol of chlorine dissolved in 2.5 ml methanol. After filtering, a bright yellow solution resulted, from which the complex crystallized on standing in a refrigerator. Yield, 1.72 g (70 % based on $C_6H_5TeTeC_6H_5$). It may be recrystallized from a warm solution of selenourea in methanol. M.p., 169° (dec.). (Found: C 19.86; H 2.65; N 11.56. Calc. for $C_8H_{13}N_4ClSe_2Te$: C 19.75; H 2.67; N 11.52).

The crystals form yellow, triclinic prisms with $a=11.22$ Å, $b=12.06$ Å, $c=5.91$ Å, $\alpha=98.95^\circ$, $\beta=93.86^\circ$, $\gamma=62.17^\circ$. With two formula units in unit cell, the calculated density is 2.30, found 2.28 g/cm³.

The complex was also prepared from $C_6H_5Te(su)Cl$ and selenourea. About 0.2 g of selenourea was dissolved in a mixture of 5 ml water, 5 ml methanol, and 0.5 ml conc. hydrochloric acid. About 0.2 g of selenourea-benzenetellurenyl chloride was added and the mixture was heated until all had dissolved. A mixture of triselenourea dichloride hydrate⁶ and diselenourea-benzenetellurenyl chloride crystallized on standing. When prepared in this way, the crystals of diselenourea-benzenetellurenyl chloride were orthorhombic long needles extended along the *c* axis, with $a=11.99$ Å, $b=21.24$ Å, $c=5.89$ Å. There are four formula units per unit cell; density, calc. 2.15, found 2.14 g/cm³. The space group, from systematic absences, is $P2_12_12_1$ (No. 19). In this form, the crystals are isomorphous with those of the corresponding thiourea complex.¹

Tetramethylammonium phenyldiselenocyanatellurate(II), $(CH_3)_4NC_6H_5Te(SeCN)_2$. To a solution of 1.25 mmol (0.50 g) of diphenylditelluride and 10 mmol (1.79 g) of tetramethylammonium selenocyanate in 30 ml of warm methanol, was added, under vigorous stirring, 1.25 mmol of bromine dissolved in 2 ml of

methanol. After filtering, a clear orange-red solution resulted, from which the tellurate(II) crystallized on standing. Yield, 0.95 g (78 %). The compound can be recrystallized from a solution of tetramethylammonium selenocyanate in methanol. M.p., 134° (dec.). (Found: C 29.79; H 3.47; N 8.72; Se 30.06. Calc. for $C_{12}H_{17}N_3Se_2Te$: C 29.48; H 3.48; N 8.60; Se 32.33).

The crystals form orange-red prisms and plates. The prisms are extended along the *b* axis, with $a=15.84$ Å, $b=9.34$ Å, $c=23.38$ Å, $\beta=100.7^\circ$. There are eight formula units in the unit cell; density, calc. 1.87, found 1.86 g/cm³. The space group, from systematic absences, is Cc (No. 9) or $C2/c$ (No. 15).

Tetramethylammonium phenyldithiocyanatellurate(II), $(CH_3)_4NC_6H_5Te(SCN)_2$, was prepared in the same way as the analogous selenocyanate complex, using 10 mmol (1.32 g) of tetramethylammonium thiocyanate. The crystals were washed with minute amounts of cold water, cold ethanol, and finally with ether, whereby co-precipitated $(CH_3)_4NSCN$ was removed. Yield, 0.64 g (65 %). M.p., 108° (dec.). (Found: C 36.34; H 4.34; N 10.43; S 16.18. Calc. for $C_{12}H_{17}N_3S_2Te$: C 36.49; H 4.31; N 10.64; S 16.22).

The crystals are isomorphous with those of the selenocyanate complex, and show the same colour and morphology. The unit cell dimensions are, $a=15.78$ Å, $b=9.18$ Å, $c=23.15$ Å, $\beta=100.6^\circ$, and density, calc. 1.59, found 1.58 g/cm³.

Tetramethylammonium phenyltetrabromotellurate(IV), $(CH_3)_4NC_6H_5TeBr_4$. In an attempt to prepare tetramethylammonium phenyldibromotellurate(II), 2.5 mmol (1.025 g) of diphenylditelluride was dissolved in 15 ml methanol, and 6.9 mmol (1.05 g) of tetramethylammonium bromide was dissolved in 10 ml of water and a small amount of hydrobromic acid, and the two solutions were mixed. 2.5 mmol of bromine dissolved in 2.5 ml methanol was added with stirring. The orange-red solution was stored in a refrigerator for 12 h. Bright yellow crystals had formed which later were shown to be tetramethylammonium phenyltetrabromotellurate(IV). Yield, 0.41 g, or 83 % based on the amount of bromine employed. M.p., 290° (dec.). (Found: C 20.19; H 2.92; N 2.47; Br 53.55. Calc. for $C_{10}H_{17}NBr_4Te$: C 20.06; H 2.84; N 2.34; Br 53.43).

Some diphenylditelluride was isolated from the mother liquor after evaporation.

The crystals of the phenyltetrabromotellurate(IV) are triclinic plates with $a=13.08$ Å, $b=15.85$ Å, $c=9.33$ Å, $\alpha=91.3^\circ$, $\beta=104.4^\circ$, $\gamma=104.8^\circ$. The density, calc. for four formula

units in the unit cell, is 2.30, found 2.29 g/cm³.

Bis(benzenetellurenyl) selenide, (C₆H₅Te)₂Se. To a solution of 2.5 mmol (1.025 g) diphenylditelluride and 10 mmol (1.44 g) of potassium selenocyanate dissolved in 30 ml of warm methanol was added, under vigorous stirring, 2.5 mmol of bromine dissolved in 2 ml methanol. The solution was stored in a refrigerator for 24 h. The blue-violet crystals of (C₆H₅Te)₂Se were then filtered off. Yield, 1.18 g, or 97 % based on the amount of diphenylditelluride employed. M.p., 64°. (Found: C 30.45; H 2.32; Se 16.42. Calc. for C₁₂H₁₀SeTe₂: C 29.50; H. 2.03; Se 16.18).

The crystals are monoclinic, and form long thin needles.

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Loroxanthin from *Chlamydomonas reinhardtii*

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Previous workers¹⁻³ have identified the main carotenoid pigments of the green alga *Chlamydomonas reinhardtii* as β -carotene, lutein, violaxanthin, trollein and neoxanthin. We have now reinvestigated the carotenoids of *Chl. reinhardtii*, strain No. 11-32 (90) from the algal collection of the Institute of Plant

Physiology, University of Göttingen, Germany.

Pigments were extracted from the damp-dried algal mass with acetone/methanol (2/1) mixtures, the total extract taken to dryness under reduced pressure and after saponification with methanolic KOH, the carotenoids were separated by thin layer chromatography on Kieselgel G layers with acetone/petrol solvent mixtures. The pigments described by previous workers were readily recognised from their visible light absorption spectra and chromatographic properties. The total pigment content (*ca.* 1.4 mg/g wet weight) and the distribution among the individual pigments were close to those previously reported.

Mass spectrometry showed the expected molecular weights for all polyenes as judged by the observation of molecular ions (M) and ions at M-92 (P), M-106 (Q) and M-158 (T) mass units.^{4,5} These ions are formed by the extrusion of 6 or 10 consecutive C-atoms of the conjugated chain with the methyl groups carried by these atoms according to the mechanism of Fig. 1.⁶ Treatment with acidified ethanol⁷ produced the expected shifts to lower wavelength in the visible light absorption spectra of the epoxides, violaxanthin and neoxanthin. However, while acetylation, with acetic anhydride in pyridine, of lutein, violaxanthin and neoxanthin yielded the required diacetates, the triol previously described as trollein provided a triacetate. Since trollein (I) contains only two acetylatable hydroxy groups,⁸ the identity of the triol with this compound is disproved.

The triol had visible light absorption maxima at 473, 446, (423) nm in acetone and thus had a nonaene chromophore of the type found in lutein (2). Mass spectrometry of the triol, in addition to M (584), P (492=M-92), Q (478=M-106) and T (426=M-158) ions, provided an ion at *m/e* 462 (M-122). The mass spectrum of the triacetate (M=710) showed an analogous ion at *m/e* 546 (M-164). The possibility that these latter ions were Q' ions formed by species in which one of the extruded C-atoms of the chain bore a hydroxymethyl or an acetoxymethyl group, respectively, rather than a methyl group was apparent.^{9,10} The partial mass shift of the Q ion, but not of the P ion, was indicative that the substituent was at C-19 rather than at C-20.^{10,11}

Further information about the position of the hydroxy groups of the triol was