

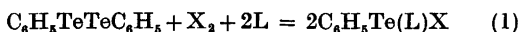
Reactions of Diphenylditelluride with Halogens in Presence of Substituted Thioureas as Ligands

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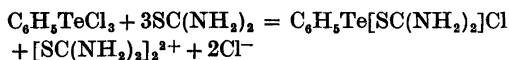
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In a recent paper, the preparation of several benzenetellurenyl halide complexes with ligands containing sulfur or selenium as donor atoms was reported.¹ The present work discusses the preparation of a series of analogous divalent tellurium compounds with ethylenethiourea (etu), trimethylenethiourea (trtu), and tetramethylthiourea (tmtu) as ligands.

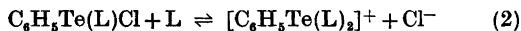
The reaction used in the preparation is:



where X_2 is chlorine or bromine, and L is a substituted thiourea. The same type of compound can also be prepared from phenyltellurium trichloride and thiourea, as follows:²



When chlorine is used in reaction (1), and the thiourea is in excess, the following equilibrium seems to be established:



With ethylenethiourea as ligand, the bis-ethylenethiourea complex was isolated in fairly good yield. When, on the other hand, tetramethylthiourea or trimethylenethiourea were used as ligands, only the complexes $\text{C}_6\text{H}_5\text{Te}(\text{L})\text{Cl}$ were isolated.

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 by the method of Haller and Irgolic.³

Bromo(ethylenethiourea)phenyltellurium(II), $\text{C}_6\text{H}_5\text{Te}(\text{etu})\text{Br}$. 1.25 mmol (0.5 g) of diphenylditelluride and 2.5 mmol (0.255 g) of ethylenethiourea were dissolved in 10 ml of warm methanol. 1.25 mmol of bromine dissolved in 2.6 ml of methanol was added. The resulting orange red solution was filtered while hot. Orange red crystals started to separate almost immediately. After about 10 min also a yellow form started to crystallize.

The pure yellow form was later obtained on seeding with the yellow crystals, but the orange red form could not be obtained pure on seeding

with the orange red crystals, in the latter case both orange red and yellow crystals deposited.

Yield of the pure yellow form, 0.97 g (83%). M.p. 142–143°C. (Found: C 28.02; H 3.02; N 7.33; S 8.35; Br 20.71. Calc. for $\text{C}_6\text{H}_5\text{N}_2\text{S}_2\text{TeBr}$: C 27.94, H 2.85, N 7.24; S 8.28; Br 20.67).

The yellow crystals are monoclinic plates, with $a=15.54$ Å, $b=9.09$ Å, $c=19.03$ Å, $\beta=114.77^\circ$. There are eight formula units per unit cell; density, calc. 2.10, found 2.11 g/cm³. The space group, from systematic absences, is Cc (No. 9) or $C2/c$ (No. 15).

The orange red crystals could be picked out and separated from the yellow ones under a microscope. M.p. 143–144°C. (Found: C 28.06; H 2.98; N 7.28; S 8.39, Br 20.64).

The orange red crystals are monoclinic prisms extended along the a axis, with $a=7.05$ Å, $b=12.78$ Å, $c=14.47$ Å, $\beta=102.3^\circ$. There are four formula units per unit cell; density, calc. 2.01, found 2.02 g/cm³. The space group, from systematic absences, is $P2_1/c$ (No. 14).

Chloro(ethylenethiourea)phenyltellurium(II), $\text{C}_6\text{H}_5\text{Te}(\text{etu})\text{Cl}$, was prepared in a similar way as the bromide, from 1.25 mmol (0.5 g) of diphenylditelluride and 2.5 mmol (0.255 g) of ethylenethiourea dissolved in 8 ml of warm methanol, by adding 1.25 mmol of chlorine dissolved in 1.92 ml of tetrachloromethane. The resulting orange red solution was filtered while hot. After 12 h in a refrigerator, the orange red crystals which had deposited were filtered off, washed with small amounts of cold methanol, then with ether, and dried. Yield, 0.68 g (79%). M.p. 133–136°C. (Found: C 31.61; H 3.28; N 8.05; S 9.25; Cl 10.42. Calc. for $\text{C}_6\text{H}_5\text{N}_2\text{S}_2\text{TeCl}$: C 31.56; H 3.21; N 8.18; S 9.35; Cl 10.36).

The crystals are isomorphous with those of the orange red form of the bromide, and have the same colour and morphology. The unit cell dimensions are, $a=7.03$ Å, $b=12.38$ Å, $c=14.39$ Å, $\beta=102.25^\circ$, and the space group, from systematic absences, is $P2_1/c$ (No. 14). Density, calc. 1.87, found 1.87 g/cm³.

Ethylenethiourea(phenyl)thiocyanatellurium(II), $\text{C}_6\text{H}_5\text{Te}(\text{etu})\text{SCN}$. To a solution of 2.5 mmol (0.255 g) of ethylenethiourea and 3.1 mmol (0.3 g) of potassium thiocyanate in 8 ml of warm water, 1.25 mmol (0.5 g) of diphenylditelluride dissolved in 8 ml of warm methanol and 1.25 mmol of chlorine dissolved in 2.1 ml of methanol were added. The resulting clear orange yellow solution was placed in a refrigerator for 12 h. Yield, 0.64 g (70%). M.p. 111–113°C. (Found: C 32.84; H 3.13; N 11.69; S 17.52. Calc. for $\text{C}_{10}\text{H}_{11}\text{N}_3\text{S}_2\text{Te}$: C 32.88; H 3.01; N 11.51; S 17.54).

The crystals are yellow orthorhombic needles extended along the c axis, with $a=11.58$ Å, $b=16.97$ Å, $c=6.83$ Å. There are four formula units per unit cell; density, calc. 1.80, found 1.80 g/cm³. The space group, from systematic absences, is $P2_12_12$ (No. 18).

The compound was also prepared by adding

a solution of 2.06 mmol (0.2 g) of potassium thiocyanate in 5 ml of warm water to a solution of 1 mmol (0.34 g) of ethylenethiourea-benzenetellurenyl chloride in 5 ml of warm methanol. The resulting clear orange yellow solution was placed in a refrigerator for 12 h. Yield, 0.32 g (88 %). M.p. 112–113 °C. The compound was identified by its melting point and by X-ray photographs.

Chlorobis(ethylenethiourea)phenyltellurium-(II), $C_6H_5Te(etu)_2Cl$. 1.25 mmol (0.5 g) of diphenylditelluride and 5.88 mmol (0.6 g) of ethylenethiourea were dissolved in 10 ml of warm methanol. 1.25 mmol of chlorine dissolved in 1.92 ml of tetrachloromethane was added. The resulting orange yellow solution was filtered while hot, and placed in a refrigerator for 6 h. Yield, 0.89 g (80 %). M.p. 166–167 °C. (Found: C 32.46; H 3.93; N 12.53; S 14.56; Cl 8.01. Calc. for $C_{12}H_{17}N_4S_2TeCl$: C 32.42; H 3.83; N 12.61; S 14.41; Cl 7.98).

The compound forms yellow tetragonal crystals, with $a=b=10.30$ Å, $c=32.42$ Å. There are eight formula units per unit cell; density, calc. 1.72, found 1.71 g/cm³. The space group, from systematic absences, is $P4_2,2$ (No. 92) or $P4_2,2$ (No. 96).

The compound was also prepared by adding a solution of 1 mmol (0.34 g) of ethylenethiourea-benzenetellurenyl chloride in 5 ml of warm methanol to a solution of 2.94 mmol (0.3 g) of ethylenethiourea in 5 ml of warm water and 2 drops of conc. hydrochloric acid. The resulting clear orange yellow solution was placed in a refrigerator for 8 h. Yield, 0.43 g (97 %). M.p. 166–167 °C. The compound was identified by its melting point and by X-ray photographs.

Bromo(phenyl)trimethylenethioureatellurium-(II), $C_6H_5Te(trtu)Br$, was prepared using 1.25 mmol (0.5 g) of diphenylditelluride and 2.58 mmol (0.3 g) of trimethylenethiourea dissolved in 10 ml of warm methanol. 1.25 mmol of bromine dissolved in 2.6 ml of methanol was added. The resulting clear orange yellow solution was placed at room temperature for 4 h. Yield, 0.86 g (86 %). M.p. 159–160 °C. (Found: C 30.06; H 3.38; N 6.82; S 8.07; Br 20.01. Calc. for $C_{10}H_{13}N_3STeBr$: C 29.96; H 3.25; N 6.99; S 7.99; Br 19.95).

The compound forms yellow monoclinic crystals, with $a=9.09$ Å, $b=15.81$ Å, $c=10.48$ Å, $\beta=120.2^\circ$. There are four formula units per unit cell; density, calc. 2.04, found 2.04 g/cm³. The space group, from systematic absences, is $P2_1/c$ (No. 14).

Chloro(phenyl)trimethylenethioureatellurium-(II), $C_6H_5Te(trtu)Cl$, was prepared in the same way as the bromide, using 1.25 mmol (0.5 g) of diphenylditelluride and 2.58 mmol (0.3 g) of trimethylenethiourea dissolved in 9 ml of warm methanol. 1.25 mmol of chlorine dissolved in 1.92 ml of tetrachloromethane was added to the warm solution. The resulting orange red

solution was filtered while hot, and placed in a refrigerator for 8 h. Yield, 0.63 g (71 %). M.p. 165–166 °C. (Found: C 33.81; H 3.73; N 8.01; S 9.07; Cl 9.93. Calc. for $C_{10}H_{13}N_3STeCl$: C 33.70; H 3.65; N 7.86; S 8.99; Cl 9.96).

The crystals are orange red monoclinic plates, with $a=7.40$ Å, $b=10.76$ Å, $c=8.74$ Å, $\beta=114.8^\circ$. There are two formula units per unit cell; density, calc. 1.87, found 1.86 g/cm³. The space group, from systematic absences, is $P2_1$ (No. 4) or $P2_1/m$ (No. 11).

Bromo(phenyl)tetramethylthioureatellurium-(II), $C_6H_5Te(tmtu)Br$, was prepared using 1.25 mmol (0.5 g) of diphenylditelluride and 2.5 mmol (0.33 g) of tetramethylthiourea dissolved in 15 ml of warm methanol. 1.25 mmol of bromine dissolved in 2.6 ml of methanol was added to the solution. The resulting orange red solution was filtered while hot, and placed in a refrigerator for 12 h. Yield, 0.6 g. The volume of the mother liquor was reduced to half its volume. After 12 h in a refrigerator, an additional 0.25 g of the compound was isolated. Total yield, 0.85 g (82 %). M.p. 115–116 °C. (Found: C 31.66; H 4.10; N 6.67; S 7.67; Br 19.23. Calc. for $C_{11}H_{17}N_2STeBr$: C 31.69; H 4.08; N 6.72; S 7.69; Br 19.19).

The compound forms orange red monoclinic crystals, with $a=7.76$ Å, $b=12.77$ Å, $c=15.90$ Å, $\beta=108^\circ$. There are four formula units per unit cell; density, calc. 1.88, found 1.87 g/cm³. The space group, from systematic absences, is $P2_1/c$ (No. 14).

Chloro(phenyl)tetramethylthioureatellurium-(II), $C_6H_5Te(tmtu)Cl$, was prepared as described for the bromide, using 1.25 mmol (0.5 g) of diphenylditelluride and 2.5 mmol (0.33 g) of tetramethylthiourea dissolved in 10 ml of warm methanol, and 1.25 mmol of chlorine dissolved in 1.92 ml of tetrachloromethane. The resulting clear orange red solution was placed in a refrigerator for 8 h. Yield, 0.59 g (63 %). M.p. 111–113 °C. (Found: C 35.49; H 4.54; N 7.55; S 8.52; Cl 9.55. Calc. for $C_{11}H_{17}N_2STeCl$: C 35.46; H 4.57; N 7.52; S 8.60; Cl 9.52).

The crystals are isomorphous with those of the bromide and have the same colour and morphology. The unit cell dimensions are, $a=7.70$ Å, $b=12.54$ Å, $c=15.85$ Å, $\beta=109.2^\circ$, and the space group, from systematic absences, is $P2_1/c$ (No. 14). Density, calc. 1.71, found 1.71 g/cm³.

The tetramethylthiourea complexes were examined in solution by NMR spectroscopy. The NMR spectra were recorded at ambient probe temperature (ca. 30 °C) on a JEOL-C-60H spectrometer. TMS was used as internal reference and lock signal. The spectra were recorded at 54 Hz sweep width. Chemical shifts were determined using a frequency counter. The chemical shifts are accurate to within ± 0.1 Hz.

The methyl groups of tetramethylthiourea in the free ligand as well as in the complexes,

are equivalent on the NMR time scale. For tetramethylthiourea itself, the chemical shift was δ 3.08 in chloroform and δ 3.03 in dichloromethane. For $C_6H_5Te(tmtu)Br$ upfield shift to δ 3.05 in chloroform and δ 3.02 in dichloromethane were observed, while $C_6H_5Te(tmtu)Cl$ displayed shifts of δ 3.04 in chloroform and δ 3.01 in dichloromethane.

Addition of tetramethylthiourea to freshly prepared solutions of the two complexes resulted in one sharp peak of intermediate chemical shift. An exchange, rapid on the NMR time scale, between coordinated and free tetramethylthiourea evidently takes place.

1. Hauge, S. and Vikane, O. *Acta Chem. Scand.* 27 (1973) 3596.
2. Foss, O. and Hauge, S. *Acta Chem. Scand.* 13 (1959) 2155.
3. Haller, W. S. and Irgolic, K. J. *J. Organometal. Chem.* 38 (1972) 97.

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Reactions of Diphenylditelluride with Halogens in Presence of Substituted Selenoureas as Ligands

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Three-coordinated complexes of divalent tellurium containing thioureas as ligands are well known.¹⁻³ Far less known are the analogous complexes of divalent tellurium containing selenoureas as ligands.

The present paper discusses the preparation of some complexes of divalent tellurium with the formula $C_6H_5Te(L)X$ where L is ethyleneselenourea (esu), tetramethylselenourea (tmsu), or trimethyleneselenourea (trsu), and X is chlorine or bromine; also a complex $C_6H_5Te(esu)_2Cl$ has been prepared.

The selenourea complexes were prepared in the same way as the thiourea analogues,^{1,2} from diphenylditelluride, chlorine or bromine and the suitable selenourea. Diphenylditelluride was prepared by the method of Haller and Irgolic.⁴ Tetramethylselenourea, ethyleneselenourea, and trimethyleneselenourea were prepared as described by Klayman and Griffin,⁵ using the corresponding thiourea, iodomethane,

selenium, and sodium borohydride in methanol. The crude products were recrystallized as described in the literature.^{5,6}

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

Bromo(phenyl)tetramethylselenoureatellurium-(II), $C_6H_5Te(tmsu)Br$. 1.25 mmol (0.5 g) of diphenylditelluride and 2.5 mmol (0.45 g) of tetramethylselenourea were dissolved in 30 ml of warm methanol. 1.25 mmol of bromine dissolved in 2.58 ml methanol was added. After filtering, the resulting clear orange red solution was placed at room temperature over night. Yield, 0.92 g (80%). M.p. 162–163°C. (Found: C 28.44; H 3.72; N 6.11; Br 17.31. Calc. for $C_{11}H_{13}N_3SeTeBr$: C 28.51; H 3.67; N 6.04; Br 17.24).

The compound forms orange-red monoclinic prisms extended along the *a* axis, with $a = 7.71$ Å, $b = 13.06$ Å, $c = 16.17$ Å, $\beta = 108.2^\circ$. There are four formula units per unit cell; density, calc. 1.99, found 1.99 g/cm³. The space group, from systematic absences, is $P2_1/c$ (No. 14). The crystals are isomorphous with the corresponding tetramethylthiourea complex, and shows the same colour and morphology.³

Chloro(phenyl)tetramethylselenoureatellurium-(II), $C_6H_5Te(tmsu)Cl$, was prepared in the same way as the bromide, using 1.25 mmol (0.5 g) of diphenylditelluride and 2.5 mmol (0.45 g) of tetramethylselenourea dissolved in 15 ml warm methanol and adding 1.25 mmol of chlorine dissolved in 2.35 ml tetrachloromethane. The mixture was filtered while hot and the resulting clear orange-red solution was placed at room temperature for 12 h. Yield, 0.77 g (73%). M.p. 151–152°C. (Found: C 31.52; H 3.98; N 6.98; Cl 8.52. Calc. for $C_{11}H_{11}N_3SeTeCl$: C 31.48; H 4.05; N 6.68; Cl 8.46).

The crystals are isomorphous with those of the bromide, and shows the same colour and morphology. The unit cell dimensions are, $a = 7.69$ Å, $b = 12.80$ Å, $c = 15.93$, $\beta = 109.2^\circ$. Density, calc. 1.88, found 1.87 g/cm³.

Bromo(ethyleneselenourea)phenylditellurium-(II), $C_6H_5Te(esu)Br$, was prepared in a similar way as the compounds mentioned above, using 1.25 mmol (0.5 g) of diphenylditelluride and 2.5 mmol (0.37 g) of ethyleneselenourea dissolved in 10 ml warm methanol, adding 1.25 mmol of bromide dissolved in 2.58 ml methanol. The resulting clear orange-red solution was placed at room temperature for 3 h. Yield, 0.87 g (80%). M.p. 163–164°C. (Found: C 24.87; H 2.61; N 6.39; Br 18.51. Calc. for $C_9H_{11}N_3SeTeBr$: C 24.92; H 2.54; N 6.46; Br 18.43).

The compound forms orange-red monoclinic prisms extended along the *a* axis, with $a = 7.20$