

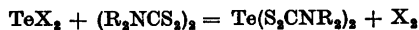
Reactions of *Bis*(thiocarbamyl)
Disulphides with Divalent
Selenium and Tellurium Thio-
sulphonates, Thiosulphates and
Xanthates

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The nucleophilic reactivities of thio anions, in displacements on divalent selenium and tellurium, increase in the order methanethiosulphonate, aromatic thiosulphonate, thiosulphate, xanthate and dithiocarbamate anions¹⁻⁶. That is, the nucleophilic reactivities of the thio anions increase with decreasing oxidizing capacity of the corresponding thio pseudohalogens. Thus, dithiocarbamate anions react with divalent selenium and tellurium thiosulphonates, thiosulphates and xanthates, to displace the thio groups and giving divalent selenium and tellurium dithiocarbamates¹⁻⁶.

It has now been found that also *bis*(thiocarbamyl) disulphides react with these compounds, to give the same selenium and tellurium derivatives. In this case, the original thio groups are converted to the corresponding thio pseudohalogens, thus:



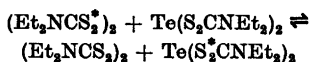
Here, X represents methanethiosulphonate, aromatic thiosulphonate, thiosulphate and xanthate, and R_2N - is dimethylamino, diethylamino or piperidyl. In these reactions, the *bis*(thiocarbamyl) disulphides thus displace thio groups having higher oxidizing properties than themselves.

This behaviour must be due to a particularly high thermodynamic stability of the divalent selenium and tellurium dithiocarbamates.

The experiments were made with divalent selenium and tellurium methane- and benzenethiosulphonate and methylxanthate in chloroform solutions, by heating for a few minutes with a slight excess of the disulphide. In the case of the thiosulphates, the sodium salts were used, with methanol containing about 15 % of water and about 15 % of chloroform as a solvent.

Bis(xanthyl) disulphides do not react with the divalent selenium and tellurium thiosulphates or thiosulphonates, nor does tetrathionate react with the thiosulphonates. The difference in behaviour of dithiocarbamate and other thio compounds is further exemplified by the existence of tetravalent selenium⁷ and tellurium^{8,9} dithiocarbamates, whereas thiosulphate^{1,2} and thiosulphonate^{4,5} ions react with these tetravalent elements to give the divalent compounds together with the thio pseudohalogens. The tetravalent selenium and tellurium dithiocarbamates are, though, labile with respect to rearrangement into *bis*(thiocarbamyl) disulphide and the divalent dithiocarbamates. The selenium compounds "frequently, if not usually"⁷ rearrange during the preparations, and the tellurium compounds do so on heating in solutions. The changes are not reversible; thus, *bis*(diethylthiocarbamyl) disulphide and divalent selenium and tellurium diethyldithiocarbamates do not react to give tetravalent diethyldithiocarbamates.

Bis(dimethylthiocarbamyl) disulphide, on heating with selenium and tellurium *bis*(diethyldithiocarbamate) in chloroform solutions, reacts to produce the corresponding divalent dimethyldithiocarbamates, which are less soluble and separate out. One may, by inference, conclude that exchanges probably take place also when the organic group of the *bis*(thiocarbamyl) disulphide is the same as that of the corresponding divalent selenium and tellurium derivative:



and likewise with Se instead of Te.

It appears possible that such exchanges, and the reactions named in the title of this note, proceed over tetravalent selenium and tellurium compounds as intermediates.

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2. Foss, O. *Acta Chem. Scand.* **3** (1949) 708.
3. Foss, O. *Acta Chem. Scand.* **3** (1949) 1385.
4. Foss, O. *Acta Chem. Scand.* **5** (1951) 115.
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7. Russell, W. F. *U.S.P.* 2 347 128 (1944).
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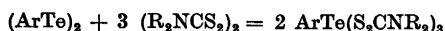
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Interactions of *Bis*(thiocarbamyl) Disulphides and *Bis*(*p*-anisyl) Ditelluride

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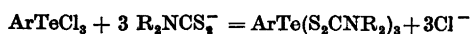
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These reactions give tetravalent tellurium compounds, as follows:



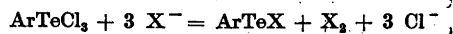
The *bis*(thiocarbamyl) disulphides here react with the ditelluride in the same way as do the halogens¹. Disulphides show halogen-like properties also in other reactions^{2, 3}.

The products, *viz.*, *p*-anisyl tellurithiocarbamates, represent a new type of organotellurium compounds. The same derivatives occur when *p*-anisyl telluritrichloride¹, in dioxane solutions, reacts with sodium dithiocarbamates:



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Thiosulphonate, thiosulphate and xanthate anions react with *p*-anisyl telluritrichloride in a different way, to give the corresponding thio pseudohalogens together with the tellurenyl compounds⁴:



The thio pseudohalogens, X₂ where X is methanethiosulphonate, aromatic thiosulphonate, thiosulphate and xanthate, do not react with *bis*(*p*-anisyl) ditelluride. The above equations thus illustrate, once more⁵, a difference in the behaviour of dithiocarbamate and these other thio groups.

The *p*-anisyl tellurithiocarbamates form stable, greenish yellow crystals, whereas ditellurides, and tellurenyl derivatives⁴, have a red colour. The preparations were made by dissolving 2.5 millimoles of *bis*(*p*-anisyl) ditelluride and 7.5 millimoles of the disulphide in 10 ml of chloroform, heating, and addition of 15–20 ml of ethanol to the mixture. On continued heating, the products crystallized in about 90 % yields. The dimethylamino derivative is sparingly soluble in cold chloroform, the diethylamino and piperidyl derivatives are readily soluble. In preheated baths, these compounds melt and decompose at approx. 184°, 156° and 178° C, respectively.

Compound (Ar = <i>p</i> -anisyl)	% Te	
	Calc.	Found
ArTe(S ₂ CN(CH ₃) ₂) ₃	21.4	21.4
ArTe(S ₂ CN(C ₂ H ₅) ₂) ₃	18.8	18.8
ArTe(S ₂ CNC ₅ H ₁₀) ₃	17.8	17.7

In chloroform, tetrachloroethane and toluene solutions, the *p*-anisyl tellurithiocarbamates possess pronounced thermochromic properties. On heating, the colour changes slowly and reversibly from greenish yellow to red. Addition of the parent *bis*(thiocarbamyl) disulphide to the hot red solutions causes the red colour to recede more rapidly on cooling. These phenomena are indications of a reversible