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Preparation and Some Reactions of Selenium and Tellurium Bis(dithiocarboxylates)

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A number of selenium- **2** and tellurium bis(dithiocarboxylates) **3** have been prepared by the reaction of piperidinium or sodium dithiocarboxylates **1** with sodium seleno- and telluropentathionates. The orange or red products are stable towards heat and moisture. It was found that **2** and **3** react with halogens and *N*-chloro- and *N*-bromosuccinimide to give the corresponding haloselenium- **4, 5** and halotellurium dithiocarboxylates **6** – **8** in good yields. The $n \rightarrow \pi^*$ transitions of the thiocarbonyl groups in **2** – **8** are observed in a region of shorter wavelengths (hypsochromic shift) than those of the corresponding bis(thioacyl) trisulfides and dithio- and thioneselenol esters.

Darstellung und einige Reaktionen von Selen- und Tellur-bis(dithiocarboxylaten)

Durch Umsetzung von Piperidinium- oder Natrium-dithiocarboxylaten **1** mit Natrium-seleno- oder -telluropentathionaten wurden die Selen- **2** und Tellur-bis(dithiocarboxylate) **3** dargestellt. Die orangefarbenen oder roten Kristalle sind thermisch stabil und nicht feuchtigkeitsempfindlich. Durch Umsetzung von **2** oder **3** mit Halogenen oder *N*-Chlor- oder *N*-Bromsuccinimid wurden Haloselen- **4, 5** und Halotellur-dithiocarboxylate **6** – **8** mit guten Ausbeuten erhalten. Die $n \rightarrow \pi^*$-Übergänge der Thiocarbonylgruppen in **2** – **8** treten bei kleineren Wellenlängen auf (hypsochrome Verschiebung) als die der entsprechenden Bis(thioacyl)-trisulfide sowie Dithio- und Thionselenolester.

In the preceding paper[1], we described the isolation and some reactions of bis(thioacyl) trisulfides. In the course of our studies concerning the synthetic application of thioacyl diphenylthiophosphinoyl sulfides, it was found that the reaction of the sulfides with tellurium tetrachloride gave tellurium bis(dithiocarboxylates) **3**[2]. These results prompted us to synthesize a series of hitherto unknown compounds of type **2** and **3** and to disclose their physical and chemical properties.

Results and Discussion

For the preparation of **2** and **3** the following three routes have been investigated: reaction of a) thioacyl diphenylthiophosphinoyl sulfides with selenium and tellurium tetrachloride, of b) piperidinium[3] or sodium dithiocarboxylates[4] **1** with selenium and tellurium tetrachloride, and reaction of c) piperidinium dithiocarboxylates with sodium seleno- and sodium telluropentathionates. After careful examination of these reactions we gave preference to route c) for the reason of ready availability of the starting compounds and easy purification of the products.

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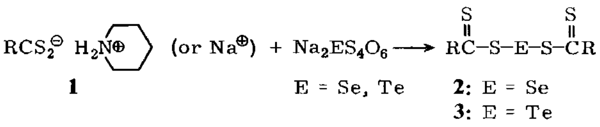


1 E = Se, Te 2: E = Se

3: E = Te (1)

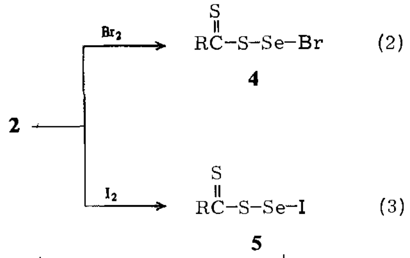
	R		R		R
2a	C_6H_5	**3a**	CH_3	**3i**	C_6H_5
b	$2\text{-}CH_3C_6H_4$	**b**	$C_6H_5CH_2$	**j**	$2\text{-}CH_3C_6H_4$
c	$4\text{-}CH_3C_6H_4$	**c**	C_2H_5	**k**	$4\text{-}CH_3C_6H_4$
d	$4\text{-}CH_3OC_6H_4$	**d**	*n*-C_3H_7	**l**	4-*tert*-$C_4H_9C_6H_4$
e	$4\text{-}ClC_6H_4$	**e**	*iso*-C_3H_7	**m**	$4\text{-}CH_3OC_6H_4$
f	$1\text{-}C_{10}H_7$	**f**	*n*-C_4H_9	**n**	$4\text{-}ClC_6H_4$
g	$2,4,6\text{-}(CH_3)_3C_6H_2$	**g**	*n*-C_5H_{11}	**o**	$1\text{-}C_{10}H_7$
		h	*cyclo*-C_6H_{11}	**p**	$2,4,6\text{-}(CH_3)_3C_6H_2$

For example, when an equimolar amount of sodium 4-(methyl)dithiobenzoate was added to an aqueous solution of sodium selenopentathionate at room temperature, an orange solid immediately precipitated which gave by recrystallization selenium bis[4-(methyl)dithiobenzoate] (**2c**) in 71% yield. Similarly, the reaction with sodium telluropentathionate gave tellurium bis[4-(methyl)dithiobenzoate] (**3k**) in 89% yield. A number of attempts to isolate aliphatic derivatives of **2** failed because of their instability and difficulty of their purification. The yields and physical properties of **2** and **3** are summarized in Table 1a. Their structures were confirmed on the basis of IR, UV/Vis, ^1H NMR, and mass spectra and elemental analyses.

The obtained aromatic selenium- **2** and tellurium bis(dithiocarboxylates) **3** are orange to dark red crystals and are stable towards heat and moisture, whereas aliphatic selenium derivatives of type **2** are less stable than the aromatic ones and, in addition, the aliphatic tellurium ones. They gradually decompose at 0°C to give selenium and an intractable oil, probably bis(thioacyl) disulfides.

The absorption maxima of the derivatives of **2** and **3** are listed in Table 1a. These selenium and tellurium bis(dithiocarboxylates) do not show any absorption maximum in the regions of both 480 – 490 nm (R = aliphatic) and 500 – 530 nm (R = aromatic), in which the $n \rightarrow \pi^*$ transitions of the thiocarbonyl group of dithioesters[3,5] and bis(thioacyl) di- and trisulfides can be observed[1]. Instead, a new characteristic absorption maximum due to the $n \rightarrow \pi^*$ transitions is observed in the regions of 420 – 430 (R = aliphatic) and 420 – 460 nm (R = aromatic), respectively. Surprisingly, their molar extinction coefficients (MEC) are unusually high ($\lg \varepsilon > 3$). To the best of our knowledge, such high MEC's have been unknown for the $n \rightarrow \pi^*$ transition of the thiocarbonyl group. It should be noted that haloselenium- **4** and **5**, halotellurium- **6** – **8** and phenyltellurium dithiocarboxylates[6] also show high MEC's as will be described later. Although no appropriate explanation for these hypsochromic and hyperchromic shifts of the $n \rightarrow \pi^*$ transition of the thiocarbonyl group has been given until now, an intramolecular coordination of the thiocarbonyl sulfur atoms to the selenium or tellurium atom[7] may be considered as one possible reason, because *Se*-aryl thioneselenol esters[8], in which the selenium atom is directly bonded to the thiocarbonyl carbons, show no hypsochromic and hyperchromic shifts compared with the corresponding dithioester. In addition, it is interesting that the $n \rightarrow \pi^*$ transition of the 2-methyl-substituted selenium derivative **2b** appears at a longer wavelength than that of the 4-methyl derivative **2c**. Presumably, coordination to the selenium atom is prevented by steric hindrance of the 2-methyl group.

It is well known that diaryl selenides and tellurides react readily with halogens to give the corresponding adducts, diarylselenium-[9] and tellurium dihalides[10]. However, **2** and **3** were found to react with halogen and *N*-chloro- (NCS) or *N*-bromosuccinimide (NBS) to give the corresponding haloselenium **4**, **5** and halotellurium dithiocarboxylates **6**–**8**.

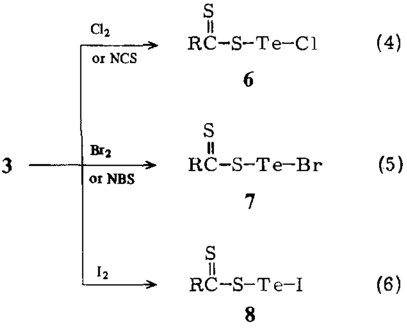


$$2 \xrightarrow{Br_2} R\overset{S}{\overset{\|}{C}}{-}S{-}Se{-}Br \quad (2)$$

4

$$2 \xrightarrow{I_2} R\overset{S}{\overset{\|}{C}}{-}S{-}Se{-}I \quad (3)$$

5



$$3 \xrightarrow[\text{or NCS}]{Cl_2} R\overset{S}{\overset{\|}{C}}{-}S{-}Te{-}Cl \quad (4)$$

6

$$3 \xrightarrow[\text{or NBS}]{Br_2} R\overset{S}{\overset{\|}{C}}{-}S{-}Te{-}Br \quad (5)$$

7

$$3 \xrightarrow{I_2} R\overset{S}{\overset{\|}{C}}{-}S{-}Te{-}I \quad (6)$$

8

	R
4a	C_6H_5
b	2-$CH_3C_6H_4$
c	4-$CH_3C_6H_4$
d	4-$CH_3OC_6H_4$
e	4-ClC_6H_4
f	1-$C_{10}H_7$

	R
5a	C_6H_5
b	4-$CH_3C_6H_4$
c	4-$CH_3OC_6H_4$
d	4-ClC_6H_4

	R
6a	C_6H_5
b	4-$CH_3C_6H_4$
c	4-$CH_3OC_6H_4$
d	4-ClC_6H_4

	R
8a	CH_3
b	4-$CH_3C_6H_4$

	R
7a	CH_3
b	C_2H_5
c	*n*-C_3H_7
d	*iso*-C_3H_7
e	*n*-C_4H_9
f	*cyclo*-C_6H_{11}

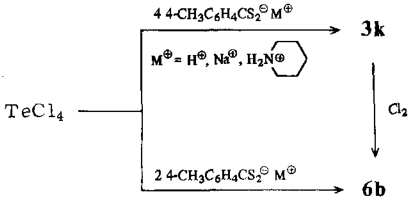
	R
7g	C_6H_5
h	2-$CH_3C_6H_4$
i	4-$CH_3C_6H_4$
j	4-*tert*-$C_4H_9C_6H_4$
k	4-$CH_3OC_6H_4$
l	4-ClC_6H_4
m	1-$C_{10}H_7$

For example, when an equimolar amount of bromine was added to selenium bis[4-(methyl)dithiobenzoate] (**2c**) in dichloromethane at 0°C, a reddish orange solid precipitated. Purification of this solid gave bromoselenium 4-(methyl)dithiobenzoate (**4c**) in 37% yield. The structure of **4c** was established on the basis of spectral data.

Thus, the IR spectrum shows two characteristic strong absorption bands at 1590 and 1295 cm^{-1} due to the aromatic ring skeletal stretching and to the thiocarbonyl stretching vibrations, respectively. In the visible region of the electron spectrum, a characteristic absorption maximum at 438 nm is observed, apparently due to the $n \rightarrow \pi^*$ transition of the thiocarbonyl group. The results of elemental analysis are consistent with the calculated values of structure **4c**.

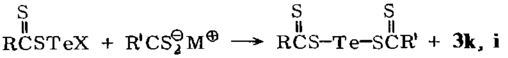
Other aromatic selenium bis(dithiocarboxylates) also reacted with bromine to give the corresponding bromoselenium dithiocarboxylates **4a**, **4b**, **4d** – **f** in moderate yields. The similar halogenation of tellurium bis(dithiocarboxylates) **3** gave the corresponding chloro- **6**[11], bromo- **7**, and iodotellurium dithiocarboxylates **8**, the yields and physical properties of which are summarized in Tables 2 and 3. In the case of chlorination, the use of *N*-chlorosuccinimide is more effective than chlorine, because of handling.

Interestingly, the reaction of tellurium tetrachloride with two molar amounts of 4-(methyl)dithiocarboxylic acid or its piperidinium salt gave **6b**. In contrast, if four molar amounts of the dithioic salt were used, **3k** was formed. By using tellurium tetrabromide, similar results were obtained. In order to confirm whether **3** is formed *via* the halotellurium dithiocarboxylates **6** – **8**, the 4-methyl derivatives **6b**, **7i**, and **8b** were reacted with piperidinium or sodium dithiocarboxylates **1'** [cf. eq. (9)]. The results are summarized in Table 4.



(7)

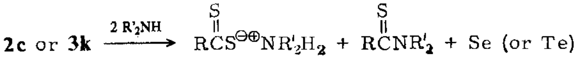
(8)



$$\mathrm{R\overset{S}{\overset{\|}{C}}STeX} + \mathrm{R'CS_2^{\ominus}M^{\oplus}} \longrightarrow \mathrm{R\overset{S}{\overset{\|}{C}}S{-}Te{-}S\overset{S}{\overset{\|}{C}}R'} + \mathbf{3k,\ i} \qquad (9)$$

6b, 7i, 8b **1'**

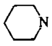
9	R	R'
a	4-$CH_3C_6H_4$	4-$CH_3OC_6H_4$
b	4-$CH_3C_6H_4$	C_6H_5



$$\mathbf{2c}\ \text{or}\ \mathbf{3k} \xrightarrow{2\ \mathrm{R'_2NH}} \mathrm{R\overset{S}{\overset{\|}{C}}S^{\ominus\oplus}NR'_2H_2} + \mathrm{R\overset{S}{\overset{\|}{C}}NR'_2} + \mathrm{Se\ (or\ Te)} \qquad (10)$$

10 **11**

1'	R'	$M^{\oplus}$
a	4-$CH_3OC_6H_4$	$^{\oplus}NH_2[CH_2]_5$
b	C_6H_5	$^{\oplus}NH_2[CH_2]_5$
c	C_6H_5	$Na^{\oplus}$
d	4-$CH_3C_6H_4$	$^{\oplus}NH_2[CH_2]_5$
e	4-(*tert*-C_4H_9)C_6H_4	$^{\oplus}NH_2[CH_2]_5$
f	4-$CH_3OC_6H_4$	$Na^{\oplus}$

	R	R'_2N
10a, 11a	4-$CH_3C_6H_4$	*cyclo*-$C_6H_{11}NH$
b, b	4-$CH_3C_6H_4$	

As shown in Table 4, the reaction with the salts possessing the same aromatic group (R = R' = $CH_3C_6H_4$) afforded high yields of the expected **3k** (run 4). If different dithioic salts (R ≠ R') were used, the expected unsymmetrical tellurium dithiocarboxylates **9** could not be isolated. The mass spectra of the reaction products, however, show the molecular ions corresponding to the unsymmetrical derivatives **9a,b**. This result suggests that tellurium bis(dithiocarboxylates) **3**, obtained by the reaction of tellurium tetrahalides with dithioic acids and their piperidinium salts, could be formed *via* the corresponding halotellurium dithiocarboxylates **6**–**8**.

In order to investigate the thioacylation ability of **2** and **3** they were reacted with primary and secondary amines. The main products were the corresponding ammonium salts **10** and thioamides **11** which are formed by decomposition of **10**.

Experimental Part

IR spectra: JASCO grating IR spectrophotometer IR-G. – UV and visible spectra: Hitachi 124 spectrometer. – ^{1}H NMR spectra (TMS as internal standard): Hitachi R-24 (60 MHz) and R-22 (90 MHz). – Mass spectra: Hitachi RMU-6M high-resolution mass spectrometer (20 eV, 150 °C). – Elemental analyses: Elemental Analysis Center of Kyoto University, Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, and A. Bernhardt, Analytisches Laboratorium (Engelskirchen, Germany).

Materials: Sodium seleno-[12] and telluropentathionate[13] were prepared by a slightly modified procedure of the literature. Selenium and tellurium tetrachlorides, chlorine, bromine, iodine, *N*-chloro- and *N*-bromosuccinimide, and triphenylphosphane were of commercial grade and were used without further purification. Preparative thin-layer chromatography (TLC) was carried out on glass plates (20 × 20 cm) coated with Wako gel BF-5. Column chromatography was performed with Wako gel C-200 and Fuji Davison silica gel BW-820 MH. Tetrahydrofuran (THF), diethyl ether, *n*-hexane, and benzene were distilled from sodium benzophenone ketyl before use. Dichloromethane and ethyl acetate were dried with calcium hydride.

General procedures for the preparation of selenium- **2** and tellurium bis(dithiocarboxylates) **3**, bromo- **4** and iodoselenium dithiocarboxylates **5**, and chloro- **6**, bromo- **7**, and iodotellurium dithiocarboxylates **8** are described below. Yields, physical properties, and microanalytical data are summarized in Tables 1a, 1b, 2a, 2b, 3a, and 3b.

Selenium bis(dithiocarboxylates) **2**: A solution of piperidinium or sodium dithiocarboxylate (2.0 mmol) was added to an aqueous solution (10 ml) containing sodium selenopentathionate (480 mg, 1.2 mmol) and the reaction mixture was stirred at room temperature for 10 min. After drying of the organic layer with magnesium sulfate, the solvent was evaporated under reduced pressure. Washing with methanol and recrystallization of the crude product from dichloromethane/*n*-hexane (**2a**–**c**, **f**, **g**) or benzene/methanol (**2d**, **e**) gave **2** as orange to reddish orange needles.

Tellurium bis(dithiocarboxylates) **3**. – *Method A:* A solution of piperidinium dithiocarboxylate (25 mmol) in water (100 ml) was added dropwise with stirring to an aqueous solution (100 ml) containing sodium telluropentathionate (10 mmol) and the reaction mixture was stirred at ca. 20 °C for 10 min (the precipitate appears immediately). Filtration, washing with water (4 × 2 ml) and finally with methanol (3 ml), and recrystallization of the crude product from dichloromethane/*n*-hexane or benzene/methanol gave tellurium bis(dithiocarboxylates) **3** as orange to dark-red crystals.

Method B: A solution of piperidinium dithiocarboxylate (25 mmol) in dichloromethane (100 ml) was added with stirring to an aqueous solution (150 ml) containing sodium telluropentathionate (15 mmol). The reaction mixture was stirred at ca. 18 °C for 10 min. After the dichloromethane layer was dried with magnesium sulfate, the solvent was evaporated under reduced pressure. Washing with methanol (5 ml) and recrystallization from the mixed solvents mentioned in Method A gave **3**.

Table 1a. Yields and physical properties of selenium- **2** and tellurium bis(dithiocarboxylates) **3**

	$(RCS_2)_2E$ (E = Se, Te)	% Yield[a] m. p.[c] [°C]	Method[b]	IR $[cm^{-1}]$[d] $\nu C{=}S$	UV/Vis [nm] λ_{max} [lg ε]
2a	Selenium bis(dithiobenzoate)	75 114 – 116		1243 1177	259 (4.39) 289 (4.46) 424 (3.59)
b	Selenium bis[2-(methyl)-dithiobenzoate]	50 71 – 75		1254 1059	309 (4.21) 513 (2.32)
c	Selenium bis[4-(methyl)-dithiobenzoate]	71 143 – 145		1250 1238 1175	257 (4.57) 297 sh 329 (4.55) 429 (3.77)
d	Selenium bis [4-(methoxy)-dithiobenzoate]	58 138 – 140		1237 1171	255 (4.74) 353 (4.69) 429 (4.00)
e	Selenium bis[4-(chloro)-dithiobenzoate]	81 155 – 156		1241 1173	257 (4.85) 309 (4.59) 432 (2.94)
f	Selenium bis(1-dithionaphthoate)	62 168 – 170		1244 1119	294 (4.40) 513 (2.29)
g	Selenium bis(2,4,6-trimethyldithiobenzoate)	32 126 – 128		1254 1160	311 (4.07) 341 sh 511 (2.19)
3a	Tellurium bis(dithioacetate)	83 130	B	1112	261 (4.77) 323 sh (3.91) 390 sh (3.38) 423 sh (2.98)
b	Tellurium bis(dithio-α-phenylacetate)	94 142	B	1110	326 sh (3.70) 401 (3.41)
c	Tellurium bis(dithiopropionate	76 58 – 59	B	1110 1145	336 sh (3.70) 389 (3.38) 424 sh (2.84)
d	Tellurium bis(dithiobutyrate)	48 59 – 60	B	1110 1148	262 (4.74) 325 sh (3.38) 423 (3.03)
e	Tellurium bis(dithioisobutyrate)	69 50 – 51	B	1150 1180	261 (4.83) 320 (4.09) 390 (3.45) 422 (3.02)
f	Tellurium bis(dithiopentanoate)	76 58 – 59	B	1110 1145	319 (3.83) 394 (3.41) 424 sh (2.84)
g	Tellurium bis(dithiohexanoate)	88 84 – 85	B	1110 1142	239 (4.46) 314 sh (3.82) 394 (3.42)
h	Tellurium bis(cyclohexanecarbodithioate)	30 122 – 123	B	1123	397 (3.44) 426 (2.94)
i	Tellurium bis(dithiobenzoate)	90 189 – 190	A	1220 1235	296 (4.59) 452 (3.89)

Table 1 a (*Continued*)

	$(RCS_2)_2E$ (E = Se, Te)	% Yield[a)] m.p.[c)] [°C]	Method[b)]	IR [cm^{-1}][d)] νC=S	UV/Vis [nm] λ_{max} [lg ε]
j	Tellurium bis[2-(methyl)-dithiobenzoate]	94 142 – 143	A	1120 1230	262 (4.77) 282 (4.72) 348 (4.06) 423 (3.70)
k	Tellurium bis[4-(methyl)-dithiobenzoate]	89 209 – 210	B	1175 1238	258 (4.71) 313 (4.61) 451 (4.71)
l	Tellurium bis[4-(*tert*-butyl)-dithiobenzoate]	99 195 – 196	B	1110 1182	258 (4.74) 316 (4.65) 451 (4.01)
m	Tellurium bis[4-(methoxy)-dithiobenzoate]	78 217 – 219	B	1170 1233 1254	345 (4.55) 458 (3.60)
n	Tellurium bis(4-chlorodithiobenzoate)	75 222 – 223	B	1175 1232	307 (4.61) 458 (4.00)
o	Tellurium bis(1-dithionaphthoate)	93 180 – 181	B	1175 1232	269 (4.76) 294 (4.59) 431 (3.85)
p	Tellurium bis(2,4,6-trimethyldithiobenzoate)	79 173 – 174	A	1000 1030	277 (4.58) 409 (3.57)

[a)] Isolated yield. – [b)] See Experimental Part. – [c)] Decomposition. – [d)] KBr. – [e)] CH_2Cl_2.

Table 1 b. Elemental analyses of selenium- **2** and tellurium bis(dithiocarboxylates) **3**

	Summation formula (Mol. mass)		C	H		Summation formula (Mol. mass)		C	H
2a[a)]	$C_{14}H_{10}S_4Se$[b)] (385.5)	Calc. Found	43.63 43.47	2.62 2.37	**3b**	$C_{16}H_{14}S_4Te$ (462.2)	Calc. Found	41.58 41.77	3.05 3.18
2b	$C_{16}H_{14}S_4Se$ (413.5)	Calc. Found	46.48 46.10	3.41 3.16	**3e**	$C_8H_{14}S_4Te$ (366.1)	Calc. Found	26.25 26.10	3.85 3.89
2c	$C_{16}H_{14}S_4Se$ (413.5)	Calc. Found	46.48 46.18	3.41 3.42	**3i**	$C_{14}H_{10}S_4Te$ (434.1)	Calc. Found	38.74 38.26	2.32 2.30
2g	$C_{20}H_{22}S_4Se$ (469.6)	Calc. Found	51.15 51.51	4.72 4.99	**3k**[a)]	$C_{16}H_{14}S_4Te$[d)] (462.2)	Calc. Found	41.58 41.89	3.05 2.89
3a[a)]	$C_4H_6S_4Te$[c)] (310.0)	Calc. Found	15.50 15.93	1.95 2.06	**3n**	$C_{14}H_8Cl_2S_4Te$ (503.0)	Calc. Found	33.43 33.06	1.60 1.51

[a)] By Analytisches Laboratorium (Germany). – [b)] Calc. S 33.27 Found 33.59; Calc. Se 20.49 Found Se 20.68. – [c)] Calc. S 41.38 Found S 41.77; Calc. Te 41.17 Found Te 41.21. – [d)] Calc. S 27.76 Found S 27.93; Calc. Te 27.61 Found Te 27.49.

***Bromoselenium dithiocarboxylates* 4**: A solution of bromine (1.2 mmol) in dichloromethane (12 ml) was added dropwise to **2** (1 mmol) in the same solvent (20 ml) at ca. 15 °C and the reaction mixture was stirred for 1 h. Removal of the solvent in a rotary evaporator, washing of the residue with carbon tetrachloride (2 × 5 ml), followed by recrystallization from dichloromethane (ca. −20 °C), gave **4** as orange red to reddish brown needles.

Iodoselenium dithiocarboxylates **5**: A solution of iodine (1.2 mmol) in dichloromethane (12 ml) was added dropwise to **2** and the reaction mixture was stirred at ca. 16 °C for 1 h. Removal of the solvent under reduced pressure, washing of the residue with carbon tetrachloride (3 × 5 ml), followed by recrystallization from dichloromethane at ca. −20 °C gave **5** as dark-red to dark-purple crystals.

Chlorotellurium dithiocarboxylates **6**. – *Method A:* Liquid chlorine [0.5 ml (710 mg), 10 mmol] was added to a solution of **3** (1.0 mmol) in dichloromethane (40 ml) at −70 °C and the reaction mixture was stirred for 1 h (the temperature was gradually raised to ca. 16 °C). Removal

Table 2a. Yields and physical properties of haloselenium dithiocarboxylates **4**, **5**

No.	Haloselenium dithiocarboxylates	% Yield[a)] m. p.[b)] [°C]	IR [cm^{-1}][c)] $\nu C=S$	UV/Vis [nm][d)] λ_{max} [lg ε]
4a	Bromoselenium dithiobenzoate	45 150–152	1283 1177	251 (4.44) 308 (4.18) 432 (3.70) 436 (3.70)
b	Bromoselenium 2-(methyl)-dithiobenzoate	38 131–134	1274 1204	252 (4.32) 309 (4.12) 404 (3.65)
c	Bromoselenium 4-(methyl)-dithiobenzoate	37 165–168	1295 1185	248 (4.46) 257 sh 438 (3.75)
d	Bromoselenium 4-(methoxy)-dithiobenzoate	56 155–156	1270 1170	250 (4.26) 349 (4.48) 444 (4.01)
e	Bromoselenium 4-(chloro)-dithiobenzoate	34 151–153	1280 1088	248 (4.48) 320 (4.23) 445 (3.77)
f	Bromoselenium 1-dithio-naphthoate	36 142–144	1245	254 (4.26) 438 (3.66)
5a	Iodoselenium dithiobenzoate	65 118–120	1288 1182	261 (4.90) 449 (3.38)
b	Iodoselenium 4-(methyl)-dithiobenzoate	71 117–130	1278 1180	270 (4.47) 342 (4.35) 442 (3.61)
c	Iodoselenium 4-(methoxy)-dithiobenzoate	68 112–114	1260 1172	258 (4.31) 273 (4.35) 364 (4.36) 451 (3.67)
d	Iodoselenium 4-(chloro)-dithiobenzoate	76 152–154	1273 1174	270 (4.40) 328 (4.35) 448 (3.57)

a) Isolated yield. – b) Decomposition. – c) KBr. – d) CH_2Cl_2.

Table 2b. Elemental analyses of haloselenium dithiocarboxylates **4**, **5**

	Summation formula (Molecular mass)		C	H	Others
4a[a]	$C_7H_5BrS_2Se$	Calc.	26.94	1.61	25.30 (Se), 25.60 (Br)
	(312.1)	Found	27.23	1.66	25.54 (Se), 25.56 (Br)
4c	$C_8H_7BrS_2Se$	Calc.	29.46	2.16	
	(326.1)	Found	29.52	2.27	
4f	$C_{11}H_7BrS_2Se$	Calc.	36.48	1.95	
	(362.2)	Found	36.63	1.99	
5a[a]	$C_7H_5IS_2Se$	Calc.	23.41	1.40	21.99 (Se), 35.34 (I)
	(359.1)	Found	23.69	1.68	22.03 (Se), 35.60 (I)
5b	$C_8H_7IS_2Se$	Calc.	25.75	1.89	
	(373.1)	Found	25.82	1.91	
5c	$C_8H_7IOS_2Se$	Calc.	24.69	1.81	
	(389.1)	Found	24.30	1.96	

[a] By Analytisches Laboratorium (Germany).

of excess chlorine and the solvent in a rotary evaporator and washing with ether (30 ml) gave **6**, which can be recrystallized from dichloromethane to yield orange to red crystals.

Method B: A solution of **3** (0.5 mmol) and *N*-chlorosuccinimide (73 mg, 0.5 mmol) in dichloromethane (100 ml) was stirred at ca. 15 °C for 1 h. Removal of the solvent under reduced pressure and washing of the residue with ethanol (3 × 10 ml) and then ether (4 × 10 ml) gave **6**.

Method C: A solution of freshly prepared dithiocarboxylic acid (ca. 0.7 mmol) in *n*-hexane (30 ml) was added to a suspension of tellurium tetrachloride (270 mg, 1.0 mmol) at −70 °C and the reaction mixture was stirred at this temperature for 3 h. Filtration and washing of the resulting precipitate with *n*-hexane (4 × 5 ml) and then ether (3 × 10 ml) gave **6**.

Method D: A solution of piperidinium 4-(methyl)dithiobenzoate (202 mg, 0.8 mmol) in dichloromethane (30 ml) was added to tellurium tetrachloride (108 mg, 0.4 mmol) at 0 °C and the reaction mixture was stirred at this temperature for 30 min. Filtration and washing of the resulting precipitate with water (5 × 3 ml), methanol (2 × 5 ml) and finally with ether (3 ml) gave chlorotellurium 4-(methyl)dithiobenzoate (**6b**).

Bromotellurium dithiocarboxylates **7**. – *Method A':* A solution of bromine (1.0 mmol) in dichloromethane (10 ml) was added dropwise with stirring to **3** (1.0 mmol) in the same solvent (10 ml for **3a** – **h** and 200 ml for **3i** – **o**) at room temperature. After stirring for 30 min, the reaction mixture was allowed to stand at ca. 20 °C for about 12 h. Filtration and washing of the resulting precipitate with carbon tetrachloride (3 × 5 ml) followed by recrystallization from dichloromethane gave **7** as reddish orange to dark-red needles.

Method B': A solution of *N*-bromosuccinimide (35 mg, 0.2 mmol) in dichloromethane (20 ml) was added to **3** (0.2 mmol) in the same solvent (40 ml) at room temperature and the reaction mixture was stirred for 1 h. Evaporation of the solvent under reduced pressure and washing of the residue with ethanol (30 ml) and then ether (2 × 20 ml) gave **7**.

Method C': A solution of freshly prepared 4-(methyl)dithiobenzoic acid (ca. 1.0 mmol) in *n*-hexane (50 ml) was added to tellurium tetrabromide (224 mg, 0.5 mmol) at 0 °C and the reaction mixture was stirred at this temperature for 30 min. Filtration and washing of the precipitate with *n*-hexane (4 × 5 ml) and then ether (2 × 10 ml) gave 220 mg (96%) of bromotellurium 4-(methyl)dithiobenzoate (**7i**).

Table 3a. Yields and physical properties of halotellurium dithiocarboxylates **6** – **8**

	Halotellurium dithiocarboxylates	Yield[a] (%)	Method[b]	m.p.[c] [°C]	IR [cm^{-1}][d] $\nu C=S$	UV/Vis [nm][e] λ_{max} [lg ε]
6a	Chlorotellurium dithiobenzoate	77 37 50	B C D	193 – 195	1255 1180	242 (4.45) 301 (4.23) 460 (3.94)
b	Chlorotellurium 4-(methyl)dithiobenzoate	39 81 51	A B D	200 – 202	1260 1180	243 (4.49) 313 (4.70) 467 (4.06)
c	Chlorotellurium 4-(methoxy)dithiobenzoate	96 62	B D	176 – 178	1265 1165	254 (4.40) 344 (4.33) 467 (4.07)
d	Chlorotellurium 4-(chloro)dithiobenzoate	65 41	B D	230 – 231	1270 1180	259 (4.59) 304 (4.54) 451 (4.52)
7a	Bromotellurium dithioacetate	62	A′	236 – 238	1168 1140	247 411
b	Bromotellurium dithiopropionate	77	A′	75 – 78	1150	247 (4.36) 411 (3.24)
c	Bromotellurium dithiobutyrate	88	A′	92 – 94	1115 1145	247 (4.48) 305 (3.80) 412 (3.36)
d	Bromotellurium dithioisobutyrate	77	A′	96 – 99	1048 1090	247 (4.45) 305 (3.48) 413 (3.35)
e	Bromotellurium dithiopentanoate	33	A′	87 – 89	1122 1152	247 (4.52) 305 (3.48) 413 (3.35)
f	Bromotellurium cyclohexanecarbodithioate	71	A′	140 – 142	1139 1166	248 (4.49) 303 (3.60) 412 (3.14)
g	Bromotellurium dithiobenzoate	45 94	A′ B′	204 – 206	1175	247 (4.36) 305 (4.22) 467 (3.93)
h	Bromotellurium 2-(methyl)dithiobenzoate	72	A′	138 – 140	1160 1195 1230	252 (4.50) 305 (4.06) 454 (3.71)
i	Bromotellurium 4-(methyl)dithiobenzoate	62 78 35	A′ B′ D′	209 – 210	1178 1256 1276	245 (4.47) 319 (4.25) 461 (3.95)
j	Bromotellurium 4-(*tert*-butyl)dithiobenzoate	99	A′	189 – 190	1105 1190 1270	246 (4.53) 322 (4.30) 471 (3.92)
k	Bromotellurium 4-(methoxy)dithiobenzoate	99 69 18	A′ B′ D′	207 – 209	1168 1255	251 (4.74) 345 (4.54) 475 (4.34)
l	Bromotellurium 4-(chloro)dithiobenzoate	66 65 17	A′ B′ D′	146 – 147	1175 1238 1268	253 (3.47) 315 (3.34) 475 (2.87)
m	Bromotellurium 1-dithionaphthoate	42	A′	175 – 177	1143 1230	258 (4.49) 460 (3.80)

Table 3a (*Continued*)

	Halotellurium dithiocarboxylates	Yield[a) (%)	Method[b)	m.p.[c) [°C]	IR [cm^{-1}][d) νC=S	UV/Vis [nm][e) λ_{max} [lg ε]
8a	Iodotellurium dithioacetate	95		144–145	1128 1158	258 311 sh 418
b	Iodotellurium 4-(methyl)dithiobenzoate	88		193–194	1175 1225 1270	259 (4.47) 329 (4.35) 482 (3.83)

a) Isolated yield. – b) A = $(RCS_2)_2Te + Cl_2$; B = $(RCS_2)_2Te$ + NCS; C = $RCS_2H + TeBr_4$; D = $RCS_2^{\ominus}\ {}^{\oplus}NH_2[CH_2]_5 + TeCl_4$; A′ = $(RCS_2)_2Te + Br_2$; B′ = $(RCS_2)_2Te$ + NBS; C′ = $RCS_2H + TeBr_4$; D′ = $RCS_2^{\ominus}\ {}^{\oplus}NH_2[CH_2]_5 + TeBr_4$. – c) Decomposition. – d) KBr. – e) CH_2Cl_2.

Table 3b. Elemental analyses of some halotellurium dithiocarboxylates **6**–**8**

	Summation formula (Mol. mass)		C	H		Summation formula (Mol. mass)		C	H
6a	$C_7H_5ClS_2Te$	Calc.	26.58	1.59	**7g**	$C_7H_5BrS_2Te$	Calc.	23.30	1.40
	(316.3)	Found	26.21	1.63		(360.8)	Found	23.33	1.46
6b	$C_8H_7ClS_2Te$[b)	Calc.	29.09	2.14	**7h**	$C_8H_7BrS_2Te$	Calc.	25.64	1.88
	(330.3)	Found	29.40	2.06		(374.8)	Found	25.27	1.86
6c	$C_8H_7ClOS_2Te$	Calc.	27.74	2.04	**7i**[a)	$C_8H_7BrS_2Te$[d)	Calc.	25.64	1.88
	(346.3)	Found	27.34	2.11		(374.8)	Found	25.61	1.83
6d	$C_7H_4Cl_2S_2Te$	Calc.	23.97	1.15	**7j**	$C_{11}H_{13}BrS_2Te$	Calc.	31.69	3.14
	(350.7)	Found	23.69	1.10		(416.9)	Found	29.20	2.89
7a[a)	$C_2H_3BrS_2Te$[c)	Calc.	8.04	1.01	**7m**	$C_{11}H_7BrS_2Te$	Calc.	32.16	1.72
	(298.7)	Found	8.15	1.10		(410.8)	Found	31.96	1.40
7b	$C_3H_5BrS_2Te$	Calc.	11.45	2.24	**8a**	$C_2H_3IS_2Te$[e)	Calc.	6.95	0.87
	(312.7)	Found	11.24	2.36		(345.7)	Found	7.02	0.89
7c	$C_4H_7BrS_2Te$	Calc.	14.70	2.16	**8b**[a)	$C_8H_7IS_2Te$[f)	Calc.	22.78	1.67
	(326.8)	Found	14.99	2.29		(421.8)	Found	22.90	1.57

a) By Analytisches Laboratorium. – b) Calc. Cl 10.73 Found Cl 10.99. – c) Calc. Br 26.75 Found Br 26.71; Calc. Te 47.72 Found Te 47.30. – d) Calc. S 17.11 Found S 16.91; Calc. Te 34.05 Found Te 33.80. – e) Calc. I 36.71 Found I 36.93. – f) Calc. Te 30.25 Found Te 30.25.

Method D′: A solution of piperidinium 4-(methyl)dithiobenzoate (127 mg, 0.5 mmol) and tellurium tetrabromide (224 mg, 0.5 mmol) in dichloromethane (30 ml) was stirred at 0 °C for 30 min. After filtration of piperidinium bromide, the filtrate was washed with water (3 × 30 ml) and dried with anhydrous sodium sulfate. Evaporation of the solvent in a rotary evaporator and washing of the residue with ether (4 × 20 ml) and then *n*-hexane (2 × 20 ml) gave 67 mg (35%) of **7i**.

Iodotellurium dithioacetate (**8a**): A solution of iodine (0.5 mmol) in dichloromethane (5 ml) was added dropwise with stirring to **3a** (155 mg, 0.5 mmol) in dichloromethane (100 ml). After stirring at ca. 12 °C for 30 min, the reaction mixture was allowed to stand at ca. –20 °C for 12 h. Filtration and washing with ethanol (8 × 5 ml) gave 164 mg (95%) of **8a**.

Iodotellurium 4-(methyl)dithiobenzoate (**8b**): A solution of iodine (0.5 mmol) in dichloromethane (5 ml) was added with stirring to **3k** (251 mg, 0.5 mmol) in the same solvent (100 ml). After stirring at ca. 15 °C for 30 min, the reaction mixture was allowed to stand at ca. −20 °C for about 12 h. Filtration, washing with ethanol (6 × 5 ml), and recrystallization from dichloromethane gave 186 mg (88%) of **8b** as dark-red needles.

Reaction of halotellurium dithiocarboxylates with piperidinium dithiocarboxylates. – Method A: A solution of piperidinium dithiocarboxylate (0.5 mmol) in dichloromethane (10 ml) was added dropwise to a suspension of halotellurium dithiocarboxylate (0.5 mmol) in the same solvent (10 ml) at ca. 10 °C and the reaction mixture was stirred for 30 min. After concentration to ca. 10 ml under reduced pressure, the concentrate was allowed to stand at −20 °C for about 12 h. Filtration of the resulting precipitate gave **3** which was confirmed by comparison of the melting points and IR spectra with those of authentic samples.

Method B: A solution of sodium dithiocarboxylate (1.0 mmol) in ethanol (10 ml) was added dropwise to a suspension of halotellurium dithiocarboxylate (1.0 mmol) in dichloromethane (10 ml). The reaction mixture was stirred at room temperature for 30 min. After washing of the dichloromethane solution with water (2 × 20 ml), the solvent was evaporated under reduced pressure. Recrystallization of the residue from dichloromethane at ca. −20 °C gave brown to dark-red needles, showing in the mass spectra the molecular-ion peaks of **3** and the unsymmetrical dithiocarboxylates **9** (all attempts to isolate **9** failed).

Table 4. Reactions of halotellurium dithiocarboxylates **6–8** with piperidinium and sodium dithiocarboxylates **1'** [cf. eq. (9)]

Run	RCS_2-TeX	$R'CS_2^{\ominus}$ $M^{\oplus}$	Method[a]	Products (M^+)[b] RC(S)STeS(S)CR' **9**	[RC(S)S]$_2$Te **3**	[R'C(S)S]$_2$Te **3**
1	**6b**	**1'a**	A	**9a** (*m/e* = 478)	**3k** (*m/e* = 462)	
2	**7i**	**1'b**	A	**9b** (*m/e* = 448)	**3k** (*m/e* = 462)	**3i** (*m/e* = 434)
3	**7i**	**1'c**	B	**9b** (*m/e* = 448)	**3k** (*m/e* = 462)	**3i** (*m/e* = 434)
4	**7i**	**1'd**	A		**3k** 93% yield	
5	**7i**	**1'e**	A		**3k** 45% yield	
6	**7i**	**1'f**	A	**9a** (*m/e* = 478)	**3k** (*m/e* = 462)	
7	**8b**	**1'f**	A	**9a** (*m/e* = 478)	**3k** (*m/e* = 462)	

[a] See Experimental Part. – [b] 180 °C, 20 eV.

Reaction of selenium bis[4-(methyl)dithiobenzoate] (**2c**) *with cyclohexylamine:* A solution of cyclohexylamine (100 mg, 1.0 mmol) in ether (10 ml) was added dropwise to a suspension of **2c** (210 mg, 0.5 mmol) in the same solvent (10 ml) and the reaction mixture was stirred at 0 °C for 3 h. A black precipitate (selenium metal, 19 mg, 40%) was filtered and the filtrate was concentrated to ca. 4 ml under reduced pressure and then *n*-hexane (5 ml) was added, followed by allowing to stand at −20 °C for about 12 h. Filtration of the resulting precipitate and washing with *n*-hexane (5 ml) gave 150 mg (56%) of cyclohexylammonium 4-(methyl)dithiobenzoate (**10a**): m.p. 96–97 °C (dec.) red needles. Chromatography of the combined filtrate and washings on silica gel [column, dichloromethane/*n*-hexane (1 : 1), yellow eluant] gave 56 mg (27%) of *N*-cyclohexyl-4-(methyl)thiobenzamide (**11a**) with m.p. 102–104 °C. The structures of **10a** and **11a** are confirmed by comparison of the IR and ^1H NMR spectra with those of authentic samples.

Reaction of tellurium bis[4-(methyl)dithiobenzoate] (**3k**) *with piperidine:* **3k** (231 mg, 0.5 mmol) and piperidine (81 mg, 1.0 mmol) were stirred in ether (20 ml) for 3 h to give 142 mg (62%)

of piperidinium 4-(methyl)dithiobenzoate (**10b**) with m.p. 116 – 118°C, 36 mg (16%) of 1-[4-(methyl)thiobenzoyl]piperidine (**11b**) with m.p. 95 – 97°C, and 43 mg (22%) of tellurium metal. The IR spectra of **10b** and **11b** were consistent with those of authentic samples.

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