Journal of Organometallic Chemistry, 190 (1980) 363—369

MERCAPTO ACID COMPOUNDS OF TELLURIUM(II): STABILIZATION OF TELLURIUM—SULFUR BONDED COMPOUNDS VIA INTRAMOLECULAR CHELATION

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(Received August 6th, 1979)

Summary

A series of tellurium(II) compounds of general formula $(RS)_2Te$ ($R = C_6H_5$—, 2-$C_{10}H_7$—, $HOOCCH_2CH_2$—, HOOCCH(Me)—, $HOOCCH_2$—, 2-$(HOOC)C_6H_4$—, $HOOCCH_2CH(COOH)$—, $NaOOCCH_2CH_2$—, $NH_4OOCCH_2CH_2$—) have been prepared and characterized. The tellurium compounds containing carboxylic acid or salt groups are isolated as stable, light-yellow solids which are soluble in alcohols or in water, and this stability is thought to be due to tellurium—carbonyl oxygen interactions within the molecule. Bis(benzenethio)tellurium(II) and bis(2-naphthalenethio)tellurium(II) have been synthesized and are unstable both in the solid state and in solution. Mixed derivatives containing one aryl and one sulfide bonded to tellurium ($ArTeSCH_2CH_2COOH$) have also been prepared, and the reactions of these compounds with dichlorobis(benzonitrile)-palladium(II) yield palladium complexes containing two tellurium ligands.

The interaction of mercapto acids ($HS(CH_2)_nCOOH$) with tellurium compounds was first considered in 1933 (i.e., $Te(S(CH_2)_nCOOH)_2$ products) [1], and more recent work has described the preparation and IR—Raman spectra of several such compositions [2]. Our interest in the further exploration of such complexes arose from recent work in our laboratories on the preparation and characterization of a new type of organotellurium composition [3] containing a ligand having an additional Lewis base function within the organic radical. This additional site can then coordinate to tellurium, thus enhancing stability of the complex with respect to thermal elimination of tellurium metal. Tellurium—mercapto acid compounds were considered as good candidates for this type of bonding interaction, owing to the possibility of coordination through both the sulfur and the carboxylic acid functions. This paper describes the preparation of a series of such derivatives and discusses the effect of intramolecular chelation upon the thermal stability of these types of compounds.

Experimental

These chemicals were obtained commercially: sodium tellurite (Research Organic/Research Inorganic) and tellurium dioxide (Alfa). Diphenyl ditelluride [4] and dichlorobis(benzonitrile)palladium(II) [5] were prepared as previously described. All other chemicals and solvents were obtained from Eastman Organic Chemicals. Melting points are uncorrected and were taken in air. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 567 grating IR spectrophotometer.

Preparation of bis(2-carboxyethanethio)tellurium(II)

A solution of sodium tellurite (2.22 g, 10 mmol) in 20 ml of water was added dropwise to a solution of 3-mercaptopropionic acid (6.36 g, 60 mmol) in 150 ml of water. The mixture was stirred at room temperature for 5 min, and the precipitate was filtered from the reaction mixture and dried. The resulting solid was recrystallized from ethanol to yield 2.4 g (72%) of a light-yellow solid, m.p. dec. over 95° C.

Preparation of bis(carboxymethanethio)tellurium(II)

A solution of sodium tellurite (2.22 g, 10 mmol) in 20 ml of water was added dropwise to a solution of mercaptoacetic acid (6.9 g of an 80% aqueous solution, 60 mmol) in 150 ml of water containing 2.5 ml of conc. hydrochloric acid. The reaction mixture was a clear yellow solution immediately following the addition, and a precipitate formed after stirring at room temperature for 5 min. The precipitate was filtered and dried to yield 1.4 g (45%) of a yellow solid. An analytical sample of this compound was prepared by recrystallization from water.

Preparation of bis(2-carboxybenzenethio)tellurium(II)

A solution of sodium tellurite (2.22 g, 10 mmol) in 20 ml of water was added to a solution of 2-mercaptobenzoic acid (9.25 g, 60 mmol) in 200 ml of methanol. The reaction mixture was stirred for 5 min at room temperature and filtered. The resulting solid was dissolved in a minimum of cold dimethylformamide, and the solution was filtered and mixed with four times its volume of methanol. Cooling overnight and filtration yielded 3.9 g (90%) of a yellow solid, m.p. dec. over 120° C.

Preparation of bis(benzenethio)tellurium(II)

A solution of sodium tellurite (2.22 g, 10 mmol) in 20 ml of water was added to a solution of benzenethiol (6.61 g, 60 mmol) in 2.5 ml of conc. hydrochloric acid and 200 ml of methanol. At the end of the addition the solution had become cloudy, and after 5 min more stirring at room temperature, a solid formed. The precipitate was filtered, washed well with methanol, and dried to yield 2.0 g (58%) of an orange-red solid, m.p. 67—69°C, dec. 75° C.

Bis(2-naphthalenethio)tellurium(II) was prepared in 92% yield in an analogous manner.

Preparation of bis(1-carboxyethanethio)tellurium(II)

A solution of 2-mercaptopropionic acid (10.6 g, 100 mmol) in 40 ml of water was added to a solution of tellurium dioxide (3.2 g, 20 mmol) in 20 ml of 2 *N* sodium hydroxide. The resulting yellow solution was extracted with ether (2 × 100 ml), and the ether extract was dried over anhydrous magnesium sulfate and filtered. The ether solution was reduced to dryness and the remaining oil recrystallized from ether/hexane to yield 3.3 g (98%) of a light-yellow solid, m.p. 84—86° C, orange melt.

Bis(1,2-dicarboxyethanethio)tellurium(II) was isolated in 99% yield following a similar procedure.

Preparation of the sodium salt of bis(2-carboxyethanethio)tellurium(II)

A solution of sodium hydroxide (0.8 g, 20 mmol) in 25 ml of water was added to a solution of bis(2-carboxyethanethio)tellurium(II) (3.38 g, 10 mmol) in 300 ml of warm ethanol. The solution was filtered and the volume was reduced to 200 ml. Ether (100 ml) was added to the ethanol solution and the flask was cooled. Filtration and drying of the resulting precipitate yielded 2.5 g (65%) of a light-yellow solid, m.p. dec. over 100° C.

The additional sodium or ammonium containing compounds listed in Table 1 were prepared by a similar procedure.

Preparation of 2-carboxyethanethiophenyltellurium(II)

A solution of 3-mercaptopropionic acid (1.06 g, 10 mmol) in 25 ml of ethanol was added to a solution of diphenylditelluride (2.05 g, 5 mmol) in 175 ml of ethanol. The reaction mixture was stirred at room temperature for 24 h, reduced in volume to 50 ml, and water was added until the cloudy point was reached. Cooling the solution overnight yielded a solid, which was filtered and dried to give 1.1 g (35%) of a light-yellow solid, m.p. ~40° C, red melt.

Preparation of dichlorobis(2-carboxyethanethiophenyltellurium)palladium(II)

A solution of 2-carboxyethanethiophenyltellurium(II) (0.30 g, 0.968 mmol) in 30 ml of methylene chloride was added to a solution of dichlorobis-(benzonitrile)palladium(II) (0.186 g, 0.485 mmol) in 10 ml of methylene chloride. The reaction was stirred at room temperature for 18 h and filtered, and the precipitate was washed with methylene chloride and hexane and dried to yield 0.35 g (90%) of an orange-brown solid, m.p. 138—140° C dec.

Results and discussion

Organosulfenyl-containing tellurides of general formula $Te(S(CH_2)_nCOOH)_2$ were prepared by various modifications of the two syntheses outlined in eqs. 1 and 2. In both procedures, the mercapto acid is present not only as a potential

$$TeO_3^{2-} + 2\,H^+ + 4\,HSRCOOH \rightarrow Te(SRCOOH)_2 + 3\,H_2O + (HOOCRS)_2 \qquad (1)$$

$$TeO_2 + 4\,HSRCOOH \rightarrow Te(SRCOOH)_2 + 2\,H_2O + (HOOCRS)_2 \qquad (2)$$

ligand for tellurium(II), but also as the reducing agent for reduction of the tellurium(IV) in the sodium tellurite or the tellurium dioxide starting materials. Tellurium compounds prepared by these two routes are tabulated with their analytical data and other information in Table 1.

TABLE 1

ANALYTICAL DATA FOR TELLURIUM-CONTAINING COMPOUNDS

Compound	Analysis-found (calcd.) (%)				m.p. (°C)	Recryst. Solvent	yield (%)
	C	H	S	Te			
$Te(SCH_2CH_2COOH)_2$	21.4 (21.33)	3.2 (2.98)	17.1 (18.98)	37.7 (37.77)	dec. over 95	ethanol	72
$Te(SCH(Me)COOH)_2$	22.0 (21.33)	3.6 (3.4)	18.1 (18.4)	37.3 (37.77)	84–86 orange melt	ether/hexane	98
$Te(SCH_2COOH)_2$	15.6 (15.51)	2.1 (1.95)	20.4 (20.70)	41.0 (41.19)	darkens over 120, black melt 135–140	water	45
$Te(S\text{-}o\text{-}COOH\text{-}C_6H_4)_2$	38.8 (38.75)	2.5 (2.32)	14.6 (14.78)	29.7 (29.40)	dec. over 120	DMF/methanol	90
$Te(SCH(COOH)CH_2COOH)_2$	22.3 (22.56)	3.0 (2.87)	15.2 (15.06)	29.6 (29.96)	75–80 orange melt	—	99
$Te(SCH_2CH_2COONa)_2$	18.6 (18.87)	2.5 (2.11)	16.5 (16.79)	32.7 (32.42)	dec. over 100	ethanol/ether	65
$Te(SCH_2CH_2COONH_4)_2$	19.7 (19.38)	4.4 (4.34)	16.9 (17.24)	34.3 (34.31)	dec. over 100	ethanol/ether	65
$Te(SCH_2CH_2COOH)(SCH_2CH_2COONa)$	19.9 (20.03)	2.9 (2.52)	17.6 (17.82)	35.8 (35.46)	dec. over 100	ethanol/ether	58
$C_6H_5Te(SCH_2CH_2COOH)$	34.6 (34.84)	3.1 (3.25)	10.4 (10.35)	40.8 (41.18)	40 red melt solid at 75	ethanol/water	35
$Te(SC_6H_5)_2$	41.5 (41.66)	2.9 (2.91)	18.2 (18.54)	36.4 (36.88)	67–69 red melt dec. 75	methanol wash	58
$Te(S\text{-}2\text{-}C_{10}H_7)_2$	53.5 (53.85)	3.3 (3.16)	14.0 (14.38)	28.3 (28.61)	grad. dec.	methanol wash	92
$(C_6H_5TeSCH_2CH_2COOH)_2PdCl_2$ [a]	27.1 (27.13)	2.6 (2.53)	8.5 (8.05)	32.3 (32.02)	138–141 dec.	—	90
$p\text{-}MeC_6H_4TeSCH_2CH_2COOH$	37.2 (37.09)	3.8 (3.73)	10.4 (9.90)	39.1 (39.40)	50 red melt solidifies	ethanol/water	45
$(p\text{-}MeC_6H_4TeSCH_2CH_2COOH)_2PdCl_2$ [b]	28.8 (29.12)	3.3 (2.93)	8.1 (7.77)	30.6 (30.93)	145–145 dec.	—	90

[a] Analyzed for Pd: found, 13.6, calcd. 13.35%. [b] Analyzed for Pd: found, 13.1, calcd. 12.90%

Synthesis of the tellurium compounds by eq. 1 is simple; a water solution of sodium tellurite is mixed with a water solution of the mercapto acid. The desired tellurium(II) product is then precipitated from solution (if it has low water solubility) and purified by recrystallization. Certain starting mercapto acids (e.g., 2-mercaptobenzoic acid) were not soluble enough in water, and methanol was used as the solvent. In a further modification of this procedure, the reaction was run in a stronger acid medium, achieved by adding small amounts of conc. hydrochloric acid to the reaction solution. This step proved to be essential not only for the preparation of $Te(SCH_2COOH)_2$, but also for the synthesis of the unsubstituted aryl derivatives in eq. 3. Bis(benzenethio)-

$$TeO_3^{2-} + 2\,H^+ + 4\,ArSH \rightarrow (ArS)_2Te + 3\,H_2O + (ArS)_2 \qquad (3)$$

Ar = phenyl, 2-naphthyl

tellurium(II) (orange-red) and bis(2-naphthalenethio)tellurium(II) (yellow) were isolated as very insoluble (water, methanol, chloroform, benzene) solids using this reaction variation. Both of these compounds gave excellent elemental analyses for the proposed structures; however, during a week's storage in a vial under inert atmosphere, both decomposed to black solids. Bis(benzenethio)tellurium(II) could be dissolved in dimethylformamide; however, the solution rapidly decomposed with formation of tellurium metal. Elemental analysis of these decomposed solids agreed well with the $(ArS)_2Te$ compositions, and extraction of decomposed bis(benzenethio)tellurium(II) with methylene chloride followed by filtration yielded black tellurium metal and an organic compound which melted at 58—60° C and gave a good analysis for diphenyl disulfide, thus indicating that the decomposition pathway for these compounds involves extrusion of tellurium as the metal and formation of a diaryl disulfide fragment.

The carboxylic acid-containing compounds were obtained as light-yellow solids, stable in air (although most derivatives should be stored in the cold to prevent darkening of the sample) and when recrystallized from boiling ethanol or hot water.

Examination of the infrared spectra of these compounds in the carbonyl region yielded one possible explanation (see Table 2) for the unusual stability of these compounds. Comparison of the carbonyl stretching frequencies of the free ligands with those of the tellurium-coordinated ligands showed a decrease in these bands of 10—30 cm^{-1}. This may indicate the presence of an intramolecular interaction between the tellurium and the acid carbonyl group, thus yielding a stable tellurium—ligand complex. In general, compositions containing a 5-membered tellurium—oxygen interaction decreased more in $\nu(CO)$ (30 cm^{-1}) than those containing a 6-membered association (10—15 cm^{-1}), indicating that the 5-membered ring may be more favorable for stability of the complex. This effect was also noted in the melting-point behavior of two representative compounds, $Te(SCH_2CH_2COOH)_2$ (6 member) and its isomer $Te(SCH(Me)COOH)_2$ (5 member). $Te(SCH_2CH_2COOH)_2$ decomposed in the melting-point tube, but $Te(SCH(Me)COOH)_2$ had a sharp melting point (84—86° C) to an orange melt which did not appreciably darken in the heated tube. The effect of the tellurium—oxygen interaction was also seen in a comparison of $(C_6H_5S)_2Te$ and

TABLE 2

INFRARED DATA FOR TELLURIUM-CONTAINING COMPOUNDS [a]

Compound	ν_{CO} (free ligand) (cm^{-1})	ν_{CO} (Te cpd) (cm^{-1})	$\Delta\nu_{CO}$ (cm^{-1})
$Te(SCH_2CH_2COOH)_2$	1710	1700	—10
$Te(SCH(Me)COOH)_2$	1705	1675	—30
$Te(SCH_2COOH)_2$	1710	1680	—30
$Te(S\text{-}o\text{-}COOH\text{-}C_6H_4)_2$	1670	1655	—15
$Te(SCH(COOH)CH_2COOH)_2$	1710—1620vbr	1700—1600	
$Te(SCH_2CH_2COONa)_2$		1555	
$Te(SCH_2CH_2COONH_4)_2$		1545	
$Te(SCH_2CH_2COOH)(SCH_2CH_2COONa)$	1710 (acid)	1695 (acid)	—15 (acid)
	—	1560 (salt)	—
$C_6H_5TeSCH_2CH_2COOH$	1710	1695	—15
$(C_6H_5TeSCH_2CH_2COOH)_2PdCl_2$		1700	
$p\text{-}MeC_6H_4TeSCH_2CH_2COOH$	1710	1690	—20
$(p\text{-}MeC_6H_4TeSCH_2CH_2COOH)_2PdCl_2$	—	1693	—

[a] Nujol mull.

$(o\text{-}COOH\text{-}C_6H_4S)_2Te$. Bis(benzenethio)tellurium(II) was unstable as noted above, but bis(2-carboxybenzenethio)tellurium(II) was isolated as a stable yellow solid.

The decrease in ν(CO) observed in the literature for such interactions is usually somewhat larger (e.g., 95 cm^{-1} for o-(CHO)(C_6H_5STe)C_6H_4 [5] and 70 cm^{-1} for 2-acetylcyclohexanonetellurium trichloride [4]); however, the recent X-ray crystal structure of a compound (2-(Cl_3TeCH_2CO)-6-(CH_3CO)(C_5H_3N)) prepared by Gysling [3] revealed an interaction between the tellurium and one of the carbonyl groups. The decrease in ν(CO) in this case versus the free ligand is 14 cm^{-1} (1710 to 1696 cm^{-1}).

Several reactions of $Te(SCH_2CH_2COOH)_2$ were evaluated. Reaction of the tellurium compound with halogens gave only tellurium metal, as did the reaction with thionyl chloride (reaction of thionyl chloride with organic carboxylic acids normally yields an acid chloride). The potential of $Te(SCH_2CH_2COOH)_2$ as a ligand in a transition-metal system was determined via reaction with bis(benzonitrile)palladium dichloride, and decomposition again occurred.

Preparation of carboxylic acid salts of $Te(SCH_2CH_2COOH)_2$ was successful via reaction between the tellurium compound in ethanol and a stoichiometric amount of sodium or ammonium hydroxide (eq. 4). All of these compounds

$$\begin{aligned} Te(SCH_2CH_2COOH)_2 + NaOH &\rightarrow Te(SCH_2CH_2COONa)_2 + H_2O \\ &\text{or} \\ NH_4OH &\rightarrow Te(SCH_2CH_2COONH_4)_2 \end{aligned} \qquad (4)$$

were isolated as stable, light-yellow solids by addition of ether to the filtered ethanol reaction mixture. Presumably, the stabilizing tellurium—oxygen interaction is still present in the mixed derivative $Te(SCH_2CH_2COOH)(SCH_2CH_2COONa)$ (change in ν(CO) = —15 cm^{-1}). All of these materials are extremely soluble in water.

Mixed derivatives containing one aryl and one thio group ($ArTeS(CH_2)_n$-

COOH) can also be prepared. The products shown in eq. 5 were isolated via

$$(Ar)_2Te_2 + HSCH_2CH_2COOH \rightarrow ArTeSCH_2CH_2COOH \quad (5)$$

reaction between the diaryl ditelluride and the mercapto acid in ethanol solution at room temperature and were obtained as low-melting, stable, light-yellow solids with good solubility in a variety of solvents (ethanol, ether, chloroform, benzene). The infrared spectrum of $C_6H_5TeSCH_2CH_2COOH$ and p-$MeC_6H_4TeSCH_2CH_2COOH$ showed decreases in $\nu(CO)$ of 15 cm^{-1} and 20 cm^{-1}, respectively, for the tellurium complexes versus the free mercapto acid ligand.

$ArTeSCH_2CH_2COOH$ was also evaluated as a ligand for transition-metal systems via reaction with dichlorobis(benzonitrile)palladium(II) in methylene chloride. The palladium complexes $(ArTeSCH_2CH_2COOH)_2PdCl_2$ were isolated in 90% yield as orange-brown solids with good air stability.

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