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Synthesis of Rubidium and Cesium Tellurocarboxylates and an X-Ray Structural Analysis of Heavy Alkali Metal Monochalcogenocarboxylates

Yasuyuki Kawahara, Shinzi Kato,* Takahiro Kanda, Toshiaki Murai, and Masahiro Ebihara*

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-11

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A series of rubidium and cesium tellurocarboxylates (**2** and **3**) were synthesized from the reaction of *O*-trimethylsilyl tellurocarboxylates (**1**) with rubidium and cesium fluorides in moderate isolated yields and characterized by ^{1}H, ^{13}C, and ^{125}Te NMR spectroscopy and X-ray diffraction. The carbon–oxygen distance [1.235(6) Å] of the tellurocarboxyl group of crystalline cesium 2-methoxybenzenecarbotelluroate (**3f**) showed a typical value of the carbon–oxygen double bond. The crystal packing of **3f** shows the possibility of an interaction between the cesium cation and the aromatic ring carbon. The thio- and selenocarboxyl groups of the corresponding sulfur and selenium isologues (**4** and **5**) also indicate a double bond [1.231(4) and 1.226(5) Å] between the carbon and oxygen, respectively. The salts (**2** and **3**) readily react with iodomethane to afford the corresponding *Te*-methyl tellurocarboxylates in good yields. The reaction between **3** and tetramethylammonium chloride was found to give a novel quaternary ammonium salt (**8**) of tellurocarboxylic acid, where the dihedral angle between benzene ring and the tellurocarboxyl group of **8** is ca. 90°. Crystallographic data for **3f**, **4**, **5**, and **8** are as follows. **3f**: $P2_1/n$, a=7.182(2), b=12.161(5), c=12.151(3) Å, β=92.57(2)°, V=1060.2(6) Å^3, d_{calcd}=2.479 g cm^{-3}, Z=4, R=0.035, R_{w}=0.043. **4**: $Pbca$, a=8.995(2), b=29.936(2), c=7.291(1) Å, V=1963.3(5) Å^3, d_{calcd}=2.030 g cm^{-3}, Z=8, R=0.024, R_{w}=0.021. **5**: $Pbca$, a=9.290(1), b=30.207(2), c=7.193(2) Å, V=2018.5(3) Å^3, d_{calcd}=2.284 g cm^{-3}, Z=8, R=0.029, R_{w}=0.020. **8**: $P2_12_12_1$, a=11.844(2), b=14.014(2), c=8.650(1) Å, V=1435.8(3) Å^3, d_{calcd}=1.558 g cm^{-3}, Z=4, R=0.044, R_{w}=0.047.

The chemistry of the chalcogeno isologues of carboxylic acid derivatives has been studied in great depth from synthetic, biological and theoretical points of view.[1] There have been formally 15 types of alkali metal chalcogenocarboxylates for each alkali metal (Fig. 1), which are considered to be one of the most important starting compounds for the synthesis of chalcogenocarboxylic acid derivatives. They are also compounds of great interest in a light of heteroatom-containing allylic anion system (E=C–O$^-$, E = hetero atom) in the molecule. The preparation of these alkali metal chalcogenocarboxylates has been limited to only two families, thio- and dithiocarboxylic acid salts, although the first preparation of potassium thiobenzoate was reported in 1868 by Engelhardt et al.[2] We have made an effort to prepare a series of alkali metal thio- and dithiocarboxylates for the last twenty years.[3] In contrast, alkali metal tellurocarboxylates have been little known. Previously, we attempted to prepare and isolate lithium,[4a] sodium,[4b,4c] and potassium tellurocarboxylates.[4d] Their structural analyses by X-ray diffraction, however, were prevented due to their extreme instability toward oxygen and thermally and to a difficulty concerning purification, although the synthesis and molecular structure of metal tellurolates have been extensively studied due to their potential use as precursor to II—VI materials.[5] Recently, we have found a facile preparation of rubidium and cesium selenocarbox-

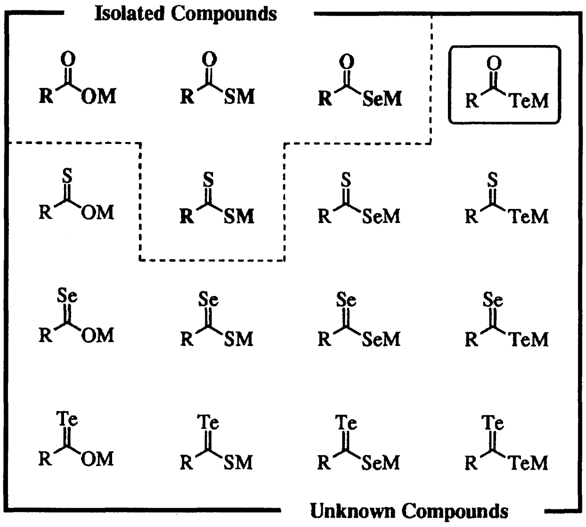
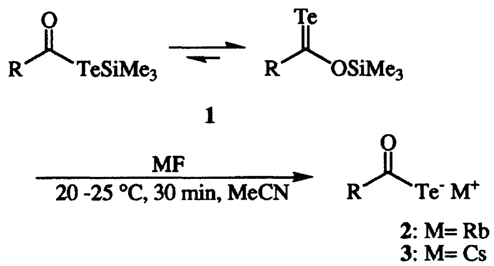


Fig. 1. Alkali metal chalcogenocarboxylates (M = Li, Na, K, Rb, Cs).

ylates by the reaction of *O*-trimethylsilyl selenocarboxylates with the corresponding metal fluorides.[6] Very recently, we succeeded in the first synthesis and isolation of two cesium tellurocarboxylates and communicated the X-ray structure analysis of cesium 2-methoxybenzenecarbotelluroate (**3f**) where the carbon–oxygen bond of the tellurocarboxyl group is close to the values of normal ester carbonyl group.[7] Here we present full details concerning the synthesis, X-ray structure analysis compared with those of the sulfur and selenium isologues and some reactions of rubidium and cesium tellurocarboxylates (**2** and **3**).

Results and Discussion

Tellurocarboxylic acids, which can act as the most suitable starting compounds for the synthesis of alkali-metal tellurocarboxylates, are too labile to be observed spectroscopically. Previously, we have found that *O*-trimethylsilyl selenocarboxylates ($RCSeOSiMe_3$) can be used as an equivalent to selenocarboxylic acids.[8] *O*-Trimethylsilyl tellurocarboxylates (**1**) (hereafter called *O*-silyl telluroesters) are also expected to be used as an equivalent to tellurocarboxylic acids. In fact, *O*-silyl telluroesters (**1**), prepared from the reaction of sodium tellurocarboxylates with trimethylsilyl chloride in acetonitrile at −10 °C, were found to readily react with rubidium and cesium fluorides to give the corresponding alkali-metal tellurocarboxylates in good yields. For example, freshly prepared *O*-silyl telluroester (**1c**) was added to an excess of rubidium fluoride at 0 °C; the mixture was then stirred in acetonitrile at room temperature, upon which the color of the solution changed from deep green to deep red. After stirring for 30 min, filtration of the excess of RbF and a trace of black tellurium, evaporation of the solvent gave rubidium benzenecarbotelluroate (**2c**) in good yield as a dark-red solid. Recrystallization from a mixed solvent of acetonitrile and ether (1 : 4) afforded 51% of pure **2c** as reddish orange plate crystals. Similarly, the reaction of the other *O*-silyl telluroesters (**1a**, **1b**, **1d**—**h**) with rubidium fluoride gave the corresponding aliphatic and aromatic rubidium tellurocarboxylates (**2a**, **2b**, **2d**—**h**) in 40—60% isolated yields (Eq. 1, Table 1). Under the same conditions, the reaction with cesium fluoride instead of rubidium fluoride provided cesium salts (**3a**—**h**) in similar yields (Table 2).



(1)

The structures of **2** and **3** were confirmed by the IR, ^1H, ^{13}C, ^{125}Te NMR spectra (Tables 1 and 2) and elemental

Table 1. Yields and Spectral Data of Rubidium Tellurocarboxylates (**2**)

	$RCOTe^-Rb^+$	Yield[a)]	IR (cm^{-1})[b)]	^{13}C NMR[c)]	^{125}Te NMR[c,d)]
No.	R	%	$\nu_{C=O}$	$\delta_{C=O}$	δ
2a	Me	46	1570	207.3	262.1
2b	*t*-Bu	44	1567	223.0	58.2
2c	C_6H_5	51	1543	208.7	228.8
2d	$2\text{-}MeC_6H_4$	42	1557	212.9	405.8
2e	$4\text{-}MeC_6H_4$	53	1541	207.8	214.0
2f	$2\text{-}MeOC_6H_4$	41	1523	208.6	435.2
2g	$4\text{-}MeOC_6H_4$	61	1547	205.9	184.3
2h	$4\text{-}ClC_6H_4$	45	1541	206.7	247.6

a) Isolated yield. b) Nujol. c) In CD_3OD. d) Standard: Me_2Te.

Table 2. Yields and Spectral Data of Cesium Tellurocarboxylates (**3**)

	$RCOTe^-Cs^+$	Yield[a)]	IR (cm^{-1})[b)]	^{13}C NMR[c)]	^{125}Te NMR[c,d)]
No.	R	%	$\nu_{C=O}$	$\delta_{C=O}$	δ
3a	Me	43	1574	207.2	286.9
3b	*t*-Bu	44	1567	223.1	80.7
3c	C_6H_5	48	1555	208.6	254.4
3d	$2\text{-}MeC_6H_4$	50	1557	212.7	419.7
3e	$4\text{-}MeC_6H_4$	54	1548	207.8	222.3
3f	$2\text{-}MeOC_6H_4$	47	1548	208.6	462.5
3g	$4\text{-}MeOC_6H_4$	59	1545	205.8	197.5
3h	$4\text{-}ClC_6H_4$	61	1546	206.6	287.8

a) Isolated yield. b) Nujol. c) In CD_3OD. d) Standard: Me_2Te.

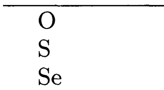
analysis.

The obtained rubidium and cesium salts (**2** and **3**) were yellow (R=aliphatic) or red to orange plate crystals (R=aryl). The metal salts (**2** and **3**) quickly decomposed at room temperature along with the liberation of black tellurium upon exposure to the air to give the corresponding rubidium and cesium carboxylates. Under an inert atmosphere, however, the aromatic derivatives were relatively stable, and no appreciable change in the color was observed, at least for one week even at 25 °C. The aliphatic derivatives were extremely unstable and quickly decomposed changing to black even below −20 °C under an argon atmosphere, and were too labile to carry out elemental analysis.

The IR and ^{13}C and ^{125}Te NMR spectra of **2** and **3** are collected in Tables 1 and 2, respectively. The carbonyl stretching frequencies appeared as the characteristic strong band in the region of 1520—1575 cm^{-1}, which were lower than those of the corresponding *Te*-alkyl esters by 80—180 cm^{-1}. The ^{13}C=O of rubidium and cesium 2,2-dimethylpropanetelluroates (**2b** and **3b**) appeared in lower field regions than those of the other derivatives,[9] while the ^{125}Te signals appeared in the upper field regions. A similar tendency was observed for ^{13}C and ^{125}Te NMR of lithium 2,2-dimethylpropanetelluroates.[4a] The ^{13}C=O signals of the aromatic derivatives were observed in the δ=205—213 region regardless of the substituents attached to the C=O group. In the ^{125}Te NMR spectra, ortho-substituted aromatic derivatives compared with unsubstituted and para-substituted ones showed the lower field shift by about δ=150—200. The similar lower field shift can be observed in ^{77}Se NMR spectra of selenium isologues.[6b] In order to compare these data, the spectral data of a series of cesium chalcogenocarboxylates are collected in Table 3. The carbonyl stretching frequencies are observed in the region of 1526—1555 cm^{-1}. The ^{13}C=O signals appear in the almost same narrow range, except for carboxylic acid salt.

Recently, it has been reported that no resonance stabilization exists in the allyl anions containing heavy heteroatom such as silicon, germanium, tin, and lead on the basis of molecular orbital calculations.[11] Furthermore, in the amides where the oxygen atom of amide is replaced by a selenium or tellurium atom, the amide forms are thermodynamically more stable than the tautomer, the imide ones.[12] It is well known that there is complete resonance between the two C–O bonds of the carboxyl group in alkali-metal carboxylates such as sodium formate.[13] The structure of the monochalcogenocarboxylate anion moiety of alkali-metal monochalcogenocarboxylates can be divided into three groups based on the localization or delocalization of the electron (Fig. 2). An X-ray diffraction analysis of metal tellurocarboxylate (**3f**) was performed so as to clarify the structure. The crystal data and data-collection parameters are collected in Table 4. An ORTEP drawing of **3f** is shown in Fig. 3, and selected bond lengths and angles are listed in Table 5. The carbon–oxygen bond length of the tellurocarboxyl group is 1.235(6) Å, being close to those of common carboxylic acid esters (1.23±0.01 Å).[14] The C–Te bond length is 2.109(6) Å, which is similar to the sp^2-carbon–tellurium single bond (ca. 2.1 Å).[15] The strong double-bond character of the carbon–oxygen bond of the tellurocarboxyl group appears to indicate that the tellurocarboxylate anion moiety of the cesium salts (**3**) in the solid state belongs to type A in Fig. 2. In general, it is widely known that a negative charge is on the more electronegative atom.[16] However, in the tellurocarboxylate anion of cesium salt

Table 3. Spectral Data of Cesium Chalcogenocarboxylates

 E	IR (cm^{-1})$^{a)}$ $\nu_{C=O}$	^{13}C NMR$^{b)}$ $\delta_{C=O}$	Ref.
O	1552	174.6	10
S	1526	213.8	3a
Se	1547	215.7	6b
Te	1555	208.6	

a) Nujol. b) CD$_3$OD.

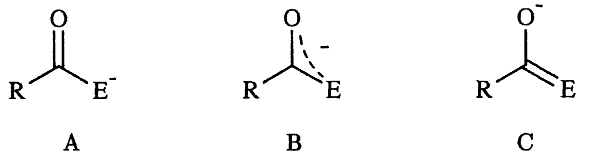


Fig. 2. The structure of monochalcogenocarboxylate anion moiety (RCOE$^-$, E=S, Se, Te).

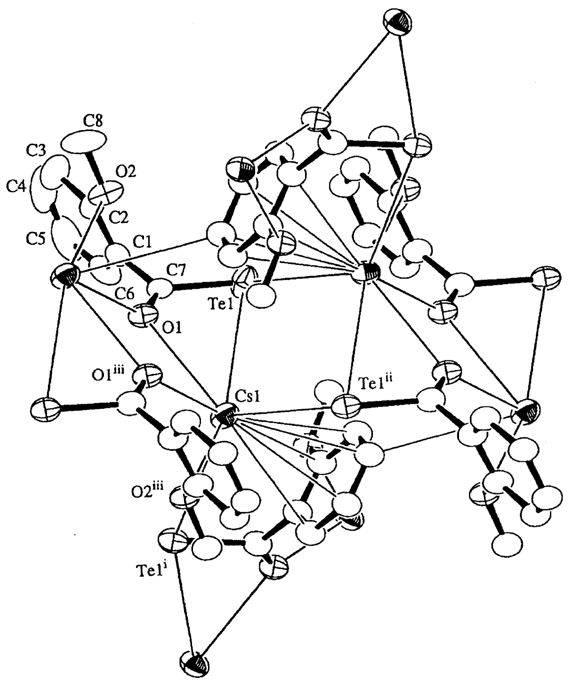


Fig. 3. Crystal packing of 2-MeOC$_6$H$_4$COTe$^-$Cs$^+$ (**3f**).

Table 4. Crystal Data and Data Collection Parameters of **3f**, **4**, **5**, and **8**

	3f	**4**	**5**	**8**
Formula	$C_8H_7CsO_2Te$	$C_8H_7CsO_2S$	$C_8H_7CsO_2Se$	$C_{12}H_{19}NO_2Te$
Formula weight	395.65	300.11	347.01	336.89
Crystal dimensions/mm	0.40×0.40×0.30	0.27×0.23×0.27	0.29×0.29×0.26	0.30×0.25×0.30
Crystal color	Orange	Colorless	Pale yellow	Yellow
Crystal shape	Needle	Needle	Needle	Needle
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$ (no.14)	$Pbca$ (no.61)	$Pbca$ (no.61)	$P2_12_12_1$ (no.19)
a/Å	7.182(2)	8.995(2)	9.290(1)	11.844(2)
b/Å	12.161(5)	29.936(2)	30.207(2)	14.014(2)
c/Å	12.151(3)	7.291(1)	7.193(2)	8.650(1)
β/deg	92.57(2)			
V/Å^3	1060.2(6)	1963.3(5)	2018.5(3)	1435.8(3)
Z	4	8	8	4
d_{calcd}/g cm^{-3}	2.479	2.030	2.284	1.558
μ(Mo $K\alpha$)/cm^{-1}	61.51	39.42	72.35	20.60
Scan type	ω–2θ	ω	ω	ω–2θ
Temp/°C	23.0	23.0	23.0	23.0
$2\theta_{\max}$/deg	55.0	55.0	55.0	55.0
Scan width/deg	$1.31+0.30\tan\theta$	$1.05+0.30\tan\theta$	$1.26+0.30\tan\theta$	$1.37+0.30\tan\theta$
Trans. coeff./min/max	0.6802/1.2246	0.9543/1.0979	0.9578/1.0262	0.7341/1.3406
No. of reflections measured	2756	2642	2709	1915
No. of observations ($I>3.0\sigma(I)$)	2048	1733	1513	1480
No. of variables	110	110	110	146
Residuals: R,[a] R_w[b]	0.035, 0.043	0.024, 0.021	0.029, 0.020	0.044, 0.047
p value[b]	0.020	0.009	0.004	0.020
Goodness of fit	2.43	1.67	1.50	2.36
Max shift/error in final cycle	0.00	0.00	0.00	0.00
Min, max peaks/e Å^{-3}	−2.33, 1.59	−0.42, 0.31	−0.48, 0.48	−0.54, 0.56

a) $R=\sum(|F_o|-|F_c|)/\sum|F_o|$. b) $R_w=[\sum(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w=[\sigma^2(F_o)+p^2(F_o)^2/4]^{-1}$.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg.) of **3f**[a]

		Bond lengths	
C(7)–O(1)	1.235(6)	Cs(1)–Te(1)$^{\mathrm{ii}}$	4.2159(8)
C(7)–Te(1)	2.109(6)	Cs(1)–O(1)$^{\mathrm{iii}}$	3.181(4)
Cs(1)–Te(1)	3.902(1)	Cs(1)–O(2)$^{\mathrm{iii}}$	3.207(4)
Cs(1)–O(1)	3.103(4)	Cs(1)···C(aromatic)$^{\mathrm{i}}$	3.591(8)—3.857(5)
Cs(1)–Te(1)$^{\mathrm{i}}$	4.136(1)		
		Bond angles	
C(1)–C(7)–O(1)	119.2(5)	C(7)–O(1)–Cs(1)	111.2(3)
C(1)–C(7)–Te(1)	115.1(3)	Te(1)–Cs(1)–O(1)	49.12(7)
O(1)–C(7)–Te(1)	125.6(4)	C(7)–C(1)–C(2)	120.6(5)
C(7)–Te(1)–Cs(1)	69.6(1)	C(7)–C(1)–C(6)	120.1(5)
		Torsion angles	
Cs(1)–Te(1)–C(7)–O(1)	19.9(4)	O(1)–C(7)–C(1)–C(2)	69.2(7)
Cs(1)–Te(1)–C(7)–C(1)	161.8(4)	O(1)–C(7)–C(1)–C(6)	112.8(6)

a) Symmetry transformations used to generate equivalent atoms: (i) $1/2-x$, $-1/2+y$, $3/2-z$, (ii) $-x$, $-y$, $1-z$, (iii) $1-x$, $-y$, $1-z$.

(**3f**), the negative charge is not on the oxygen atom, but on the tellurium atom, which is a less-electronegative atom. The crystal packing of **3f** is also unusual. The cesium ion is surrounded by three tellurium atoms, two carbonyl oxygens and one methoxy oxygen. Noteworthy is that the possibility of an interaction of the cesium cation with aromatic ring carbons of an another molecule is suggested,[17] because the distances between the Cs and aromatic carbon [3.591(8)—3.857(5) Å] are close to those of type Cs[Al$_2$Me$_6$X]•aromatic complexes (3.64—3.84 Å).[17a,17b,17c,17d] The shortest distance [Te(1)–Cs(1)] between the Te and Cs ion is 3.902(1) Å, which is close to the sum (3.91 Å) of the radii of the Te and Cs ions (Te^{2-}: 2.07 Å, Cs^{+}: 1.84 Å).[18] However, the cesium ion [Cs(1)] is found to be 1.246 Å above the plane of the tellurocarboxyl group [dihedral angle between O(1)–C(7)–Te(1) and Te(1)–Cs(1)–O(1): 156 °].

In order to compare the result with the sulfur and selenium isologues, X-ray analyses of cesium 2-methoxybenzenecarbothioate (**4**) and -carboselenoate (**5**) were carried out. The salts (**4** and **5**) are isostructural; an ORTEP drawing of **5** is shown in Fig. 4. Crystal data and data-collection parameters are collected together in Table 4. The bond lengths and angles are collected in Table 6. The carbon–oxygen bond length of the selenocarboxyl group of **5** is 1.226(5) Å. The C–Se bond length is 1.868(5) Å, which is close to the sp^2-carbon–selenium single bond (1.885—1.912 Å).[15a] In sulfur isologue (**4**), the carbon–oxygen bond length of the thiocarboxyl group is 1.231(4) Å, being close to those (1.227(4) and 1.239(4) Å) of dipotassium ethanebis(thioate)[19] and that of common esters. However, the C–S bond length (1.712(3) Å) is almost consistent with those (1.697(3) and 1.712(3) Å) of dipotassium ethanebis(thioate), and is close to the sp^2-carbon–sulfur single bonds [1.730(2)—1.770(3) Å].[1i,15a] These statements presume that the thio- and selenocarboxylate anion moieties of **4** and **5** belong to the type A, being similar to that of **3f**.[20]

The crystal packing of **4** and **5** differs markedly from that of the tellurium isologue (**3f**). In **4** and **5**, the cesium ion has no interaction with the aromatic carbon, and is surrounded by four sulfur or selenium atoms, three carbonyl oxygens and one methoxy oxygen. The shortest distance [Se(1)–Cs(1)] between the Se and Cs ions is 3.6680(7) Å, being close to the sum (3.68 Å) of the radii of the Se and Cs ions (Se^{2-}: 1.84 Å, Cs^{+}: 1.84 Å).[18] The S(1)–Cs(1) distance (3.606(1) Å) is longer than that (3.539(3) Å) of dicesium ethane(dithioate).[21]

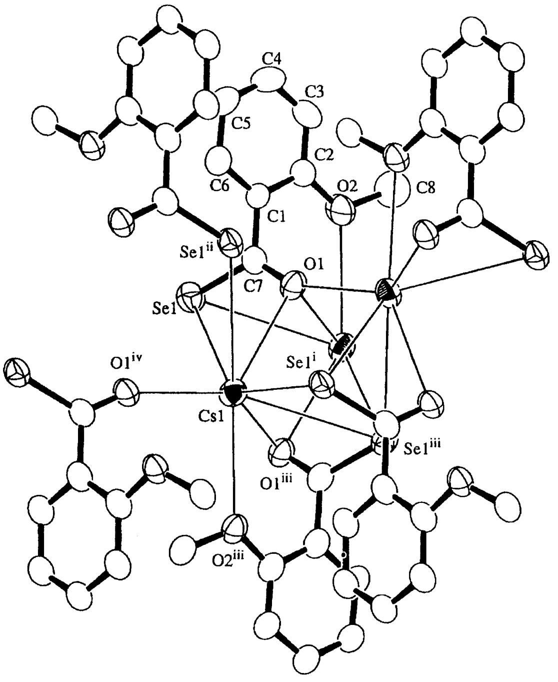


Fig. 4. Crystal packing of 2-MeOC$_6$H$_4$COSe$^-$Cs$^+$ (**5**).

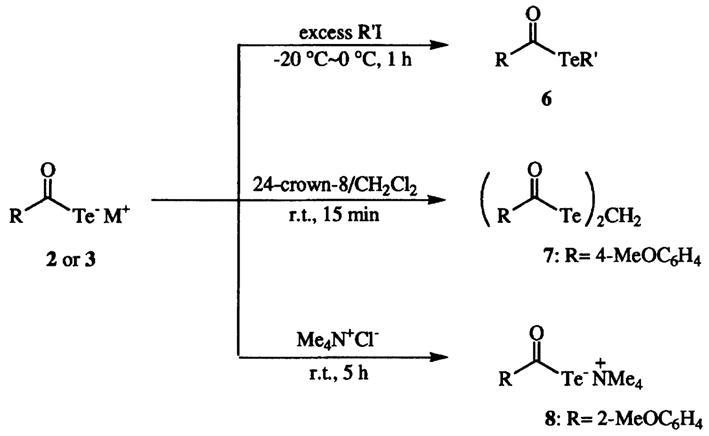
Table 6. Selected Bond Lengths (Å) and Bond Angles (deg.) of **4**$^{a)}$ and **5**$^{a)}$

	4 (E=S)	**5** (E=Se)
	Bond lengths	
C(7)–O(1)	1.231(4)	1.226(5)
C(7)–E(1)	1.712(3)	1.868(5)
Cs(1)–E(1)	3.606(1)	3.6680(7)
Cs(1)–O(1)	3.142(2)	3.239(3)
Cs(1)–E(1)^{i}	3.628(1)	3.7468(7)
Cs(1)–E(1)^{ii}	3.799(1)	3.9149(7)
Cs(1)–E(1)^{iii}	3.882(1)	3.9688(7)
Cs(1)–O(1)^{iii}	3.136(3)	3.124(3)
Cs(1)–O(1)^{iv}	2.997(3)	3.019(3)
Cs(1)–O(2)^{iii}	3.204(3)	3.223(4)
	Bond angles	
C(1)–C(7)–O(1)	118.0(3)	118.7(4)
C(1)–C(7)–E(1)	117.4(2)	117.1(3)
O(1)–C(7)–E(1)	124.7(2)	124.2(4)
C(7)–E(1)–Cs(1)	77.8(1)	77.4(1)
C(7)–O(1)–Cs(1)	104.5(2)	104.2(3)
E(1)–Cs(1)–O(1)	44.97(5)	46.44(6)
C(7)–C(1)–C(2)	121.3(3)	120.4(4)
C(7)–C(1)–C(6)	120.4(3)	120.4(4)
	Torsion angles	
Cs(1)–E(1)–C(7)–O(1)	28.0(3)	27.7(4)
Cs(1)–E(1)–C(7)–C(1)	153.8(3)	154.0(4)
O(1)–C(7)–C(1)–C(2)	55.5(5)	57.7(6)
O(1)–C(7)–C(1)–C(6)	120.4(4)	118.4(5)

a) Symmetry transformations used to generate equivalent atoms: (i) $1/2-x, -y, 1/2+z$, (ii) $-1/2+x, y, 1/2-z$, (iii) $1-x, -y, 1-z$, (iv) $1/2-x, -y, -1/2+z$.

The torsion angles [O(1)–C(7)–C(1)–C(2)] between the benzene ring and the thio- or selenocarboxyl group are 55.5(4)° and 57.7(6)°, respectively, which are smaller than that [69.2(7)°] of **3f**. The C(7)–S(1)–Cs(1) and C(7)–Se(1)–Cs(1) angles are 77.8(1)° and 77.4(1)°, being larger than the C(7)–Te(1)–Cs(1) angle [69.6(1)°]. Furthermore, the cesium ions of **4** and **5** are located out of the plane of thio- and selenocarboxyl groups by 1.654 and 1.673 Å, respectively. The dihedral angles between O(1)–C(7)–S(1) and S(1)–Cs(1)–O(1) and between O(1)–C(7)–Se(1) and Se(1)–Cs(1)–O(1) are almost the same, 147.3° and 147.7°, respectively. While, the dihedral angle of the tellurium isologue (**3f**) is wider, 156°.

The salts (**2** and **3**) easily react with the alkyl iodide to give *Te*-alkyl esters (**6**).[4b,22] Furthermore, a marked enhancement of their reactivities has been found by the addition of crown ether, which produces the naked tellurocarboxylate anion. For example, though the reaction of **3g** with dichloromethane does not occur at room temperature, the addition of an equal amount of dibenzo-24-crown-8 under identical conditions led to almost a quantitative yield of methylene bis(4-methoxybenzenecarbotelluroate) (**7**) (Scheme 1) for 15



Scheme 1.

min. Previously, we have reported on the formation of primary and secondary ammonium tellurocarboxylates from the reaction of bis(acyl) telluride with the corresponding amines.[4d)] However, this methodology can not be applied to the preparation of quaternary ammonium tellurocarboxylates ($\mathrm{RCOTeNR'_4}$). The reaction of cesium salts (**3f**) with tetramethylammonium chloride gave tetramethylammonium 2-methoxybenzenecarbotelluroate (**8**) in 77% yield. This is the first example of the preparation of quaternary ammonium chalcogenocarboxylates from a direct reaction of alkali-metal chalcogenocarboxylate with quaternary ammonium halides. The ammonium salt (**8**) is dark-red crystals, and is extremely semsitive to oxygen (Table 7). An X-ray structure analysis of quaternary ammonium chalcogenocarboxylates has not yet been performed. In order to compare the structure of **8** with cesium salt (**3f**), an X-ray crystal analysis was carried out. An ORTEP drawing is shown in Fig. 5. The carbon–oxygen bond length of the tellurocarboxyl group is 1.22(1) Å, being close to that of **3f**. It is noteworthy that the C–Te bond length is 2.09(1) Å, which is slightly shorter than that of **3f**, but still a single bond. This clearly suggests that the negative charge of **8** is on the electropositive atom, the i. e. tellurium of the tellurocarboxyl group. Furthermore, the benzene ring is nearly perpendicular to the tellurocarboxyl group [torsion angle O(1)–C(7)–C(1)–C(2): 87°]. This is probably due to the electronic repulsion between the tellurocarboxylate anion and methoxy group at the ortho position, rather than a steric repulsion, since torsion angle (69°) of **3f** is smaller than that of **8**.

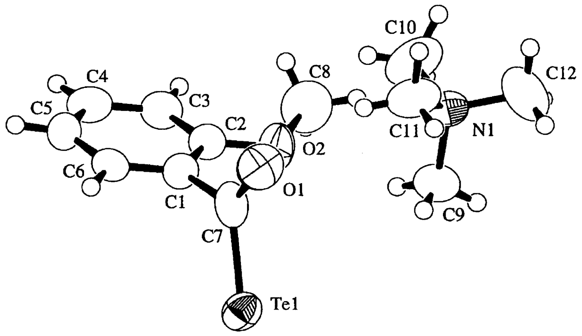


Fig. 5. ORTEP drawing of $\mathrm{2\text{-}MeOC_6H_4COTe^-Me_4N^+}$ (**8**).

In summary, rubidium and cesium tellurocarboxylates (**2** and **3**) were found to be synthesized in moderate isolated yields from the reaction of *O*-trimethylsilyl tellurocarboxylates with rubidium and cesium fluoride. This method is simple and does not require any troublesome separation of the reaction mixture. The solid-state structure of cesium tellurocarboxylate has been determined and compared with the sulfur and selenium isologues. The carbon–oxygen distances of the thio-, seleno-, and tellurocarboxyl groups ($\mathrm{-COE^-}$, E=S, Se, Te) in these salts show the values of a double bond [1.231(4),

Table 7. Selected Bond Lengths (Å) and Bond Angles (deg.) of **8**

	Bond lengths		
C(7)–O(1)	1.22(1)	N(1)···O(1)	3.74(1)
C(7)–Te(1)	2.09(1)	N(1)···Te(1)	5.601(8)
	Bond angles		
C(1)–C(7)–O(1)	118.9(10)	C(7)–C(1)–C(2)	118.0(8)
C(1)–C(7)–Te(1)	116.5(6)	C(7)–C(1)–C(6)	122.9(8)
O(1)–C(7)–Te(1)	124.4(7)		
	Torsion angles		
O(1)–C(7)–C(1)–C(2)	87(1)	O(1)–C(7)–C(1)–C(6)	90(1)

1.226(5), and 1.235(6) Å], and the carbon–chalcogen atom distances are single bonds, respectively, indicating that the negative charge is on the less electronegative chalcogen atom. The salts (**2** and **3**) can be readily alkylated by common alkylating agents such as iodomethane. The present preparation of alkali metal tellurocarboxylates would open up the possibility of preparing of a large variety of main-group and transition-metal derivatives of tellurocarboxylic acids which have been considered to be too unstable to prepare, including an acyl radical precursor of current interest[22k] as well as new synthetic reagents.

Experimental

General. The IR spectra were measured on a Perkin–Elmer FT-IR 1640. The ^{1}H NMR spectra were recorded on a JOEL JNM-GX-270 (270 MHz) with tetramethylsilane as an internal standard; the following abbreviations were used: s, singlet; d, doublet; m, multiplet. The ^{13}C NMR spectra were obtained from a JEOL JNM-GX-270 (67.9 MHz). The ^{125}Te NMR spectra were recorded on a JEOL JNM-GX-270 (85.3 MHz) with dimethyl telluride used as an external standard. Elemental analyses were carried out at the Elemental Analyses Center of Kyoto University.

Materials. Tellurium (pieces), sodium metal, rubidium fluoride, and cesium fluoride were of commercial grade, and were used without further purification. Trimethylsilyl chloride, and acetyl, pivaloyl, and benzoyl chlorides were of commercial grade and distilled before use. Other acyl chlorides (2-methyl-, 4-methyl-, 2-methoxy, 4-methoxy-, and 4-chloro-benzoyl chlorides),[23] *O*-trimethylsilyl tellurocarboxylates,[4c] and cesium 2-methoxybenzenecarbothio-,[3a] and selenoate[6b] were prepared as described in the literature. Dichloromethane and acetonitrile were distilled from phosphorus pentaoxide and degassed. Ether was distilled from sodium diphenylketyl and degassed. All of the manipulations were carried out under argon.

X-Ray Structure Analysis. All measurement were carried out on a Rigaku AFC7R diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ=0.71069 Å). All of the structures were solved and refined using the teXsan® crystallographic software package on an IRIS Indigo computer. X-Ray quality crystals of **3f**, **4**, **5**, and **8** were obtained by slow diffusion of ether into acetonitrile solutions of each of the samples. Used crystals were cut from the grown needles. Because all of the samples were unstable in air, each crystal mounted on a glass fiber was coated with an epoxy resin. The cell dimensions were determined by a least-squares refinement of the diffractometer angles for 25 automatically centered reflections. Three standard reflections were measured every 150 reflections and no decay was detected. An empirical absorption correction (DIFABS)[24] was applied. The structures were solved by direct methods [SHELX86[25]] and expanded using DIRDIF.[26] Scattering factors for neutral atoms were from Cromer and Waber[27] and anomalous dispersion[28] was used. The weighting scheme employed was $w=[\sigma^2(F_\mathrm{o})+p^2(F_\mathrm{o})^2/4]^{-1}$. A full-matrix least-squares refinement was executed with non-hydrogen atoms being anisotropic. The final least square cycle included fixed hydrogen atoms at calculated positions of which each isotropic thermal parameter was set to 1.2-times of that of the connecting atom. Crystal data and measurement description are summarized in Table 4. Tables of the atomic coordinates and anisotropic displacement parameters, bond distances, bond angles, torsion angles, least-squares planes, observed and calculated structure factors are deposited as Document No. 68062 at the Office of the Editor of Bull. Chem. Soc. Jpn.

The preparations of **2c** and **3c** are described in detail as typical procedures for rubidium and cesium salts (**2** and **3**), respectively.

Rubidium Telluroacetate (2a). Similarly to **2c**, the reaction of rubidium fluoride (0.656 g, 6.28 mmol) with *O*-trimethylsilyl telluroacetate (**1a**),[29] freshly prepared from sodium telluroacetate (0.608 g, 3.14 mmol) with trimethylsilyl chloride (0.35 mL, 3.14 mmol) in acetonitrile (10 mL), gave 0.371 g (46%) of rubidium telluroacetate (**2a**) as a yellow microcrystalline solid: IR (Nujol) 2965, 1570 (C=O), 1463, 1377, 1089, 926, 577 cm^{-1}; ^{1}H NMR ($\mathrm{CD_3OD}$) δ=2.62 (s, $\mathrm{CH_3}$); ^{13}C NMR ($\mathrm{CD_3OD}$) δ=55.3 ($\mathrm{CH_3}$), 207.3 (C=O); ^{125}Te NMR ($\mathrm{CD_3OD}$, standard $\mathrm{Me_2Te}$) δ=262.1.

Rubidium 2,2-Dimethylpropanetelluroate (2b). Similarly to **2c**, the reaction of rubidium fluoride (0.777 g, 7.44 mmol) with *O*-trimethylsilyl 2,2-dimethylpropanetelluroate (**1b**)[30] [λ 624 nm (the n–π^* transitions of C=Te)], freshly prepared from sodium 2,2-dimethylpropanetelluroate (0.878 g, 3.72 mmol) with trimethylsilyl chloride (0.40 mL, 3.72 mmol) in acetonitrile (10 mL), gave 0.483 g (44%) of rubidium 2,2-dimethylpropanetelluroate (**2b**) as a yellow microcrystalline solid: IR (Nujol) 2960, 2914, 1616, 1567 (C=O), 1455, 1404, 1378, 1353, 1220, 1029, 902, 793, 598 cm^{-1}; ^{1}H NMR ($\mathrm{CD_3OD}$) δ=1.05 (s, $\mathrm{CH_3C}$); ^{13}C NMR ($\mathrm{CD_3OD}$) δ=28.7 ($\underline{\mathrm{C}}\mathrm{H_3C}$), 55.1 ($\mathrm{CH_3}\underline{\mathrm{C}}$), 223.0 (C=O); ^{125}Te NMR ($\mathrm{CD_3OD}$, standard $\mathrm{Me_2Te}$) δ=58.2.

Rubidium Benzenecarbotelluroate (2c). To a solution of freshly prepared sodium benzenecarbotelluroate[4b] (0.682 g, 2.66 mmol) in acetonitrile (10 mL), trimethylsilyl chloride (0.29 mL, 2.66 mmol) was added at −10 °C, followed by stirring at the same temperature for 10 min. The color changed from deep red to deep green, indicating the formation of $\mathrm{PhCTeOSiMe_3}$ (**1c**) [λ 712 nm (the n–π^* transitions of C=Te)]. Rubidium fluoride (0.555 g, 5.32 mmol) was added and stirred at this temperature for 30 min (The color rapidly changed from deep green to deep red). The excesses of RbF and black tellurium were filtered out. Evaporation of the solvent in vacuo, and washing with diethyl ether (5 mL) gave 0.544 g (64% as **2c**) of a reddish-orange solid. Recrystallization from a mixed solvent of acetonitrile and diethyl ether (1 : 4) at 20 °C yielded 0.428 g (51%) of **2c** as reddish-orange plates: IR (Nujol) 2982, 2881, 1582, 1543 (C=O), 1470, 1443, 1378, 1303, 1187, 1160, 1070, 927, 873, 759, 688, 669, 600, 474 cm^{-1}; ^{1}H NMR ($\mathrm{CD_3OD}$) δ=7.28—8.03 (m, Ar); ^{13}C NMR ($\mathrm{CD_3OD}$) δ=128.1, 129.3, 132.1, 151.2 (Ar), 208.7 (C=O); ^{125}Te NMR ($\mathrm{CD_3OD}$, standard $\mathrm{Me_2Te}$) δ=228.8. Found: C, 26.22; H, 1.68%. Calcd for $\mathrm{C_7H_5ORbTe}$: C, 26.42; H, 1.58%.

Rubidium 2-Methylbenzenecarbotelluroate (2d). Similarly to **2c**, the reaction of rubidium fluoride (0.620 g, 5.92 mmol) with *O*-trimethylsilyl 2-methylbenzenecarbotelluroate (**1d**) [λ 694 nm (the n–π^* transitions of C=Te)], freshly prepared from sodium 2-methylbenzenecarbotelluroate (0.802 g, 2.97 mmol) with trimethylsilyl chloride (0.32 mL, 2.97 mmol) in acetonitrile (10 mL) and recrystallization from a mixed solvent (18 mL) of acetonitrile and ether (1 : 8), gave 0.411 g (42%) of rubidium 2-methylbenzenecarbotelluroate (**2d**) as orange plates: IR (Nujol) 2974, 2881, 1574, 1557 (C=O), 1456, 1377, 1181, 1113, 882, 855, 758, 715 cm^{-1}; ^{1}H NMR (CD_3OD) $\delta=2.33$ (3H, s, CH_3), 7.15—7.71 (4H, m, Ar); ^{13}C NMR (CD_3OD) $\delta=20.0$ (CH_3), 125.4, 128.8, 129.1, 130.0, 131.2, 156.1 (Ar), 212.9 (C=O); ^{125}Te NMR (CD_3OD, standard Me_2Te) $\delta=405.8$. Found: C, 28.58; H, 2.14%. Calcd for C_8H_7ORbTe: C, 28.92; H, 2.12%.

Rubidium 4-Methylbenzenecarbotelluroate (2e). Similarly to **2c**, the reaction of rubidium fluoride (0.457 g, 4.38 mmol) with *O*-trimethylsilyl 4-methylbenzenecarbotelluroate (**1e**)[7] [λ 700 nm (the n–π^* transitions of C=Te)], freshly prepared from sodium 4-methylbenzenecarbotelluroate (0.592 g, 2.19 mmol) with trimethylsilyl chloride (0.24 mL, 2.19 mmol) in acetonitrile (10 mL) and recrystallization from a mixed solvent (6 mL) of acetonitrile and ether (1 : 1), gave 0.388 g (53%) of rubidium 4-methylbenzenecarbotelluroate (**2e**) as reddish orange plates: IR (Nujol) 2922, 2856, 1575, 1541 (C=O), 1460, 1377, 1188, 1159, 1106, 881, 819, 782, 599, 466 cm^{-1}; ^{1}H NMR (CD_3OD) $\delta=2.27$ (3H, s, CH_3), 7.09 (2H, d, $J=8.1$ Hz, Ar), 7.92 (2H, d, $J=8.1$ Hz, Ar); ^{13}C NMR (CD_3OD) $\delta=21.4$ (CH_3), 128.8, 129.8, 142.8, 148.9 (Ar), 207.8 (C=O); ^{125}Te NMR (CD_3OD, standard Me_2Te) $\delta=214.0$. Found: C, 28.71; H, 1.95%. Calcd for C_8H_7ORbTe: C, 28.92; H, 2.12%.

Rubidium 2-Methoxybenzenecarbotelluroate (2f). Similarly to **2c**, the reaction of rubidium fluoride (0.560 g, 5.38 mmol) with *O*-trimethylsilyl 2-methoxybenzenecarbotelluroate (**1f**) [λ 670 nm (the n–π^* transitions of C=Te)], freshly prepared from sodium 2-methoxybenzenecarbotelluroate (0.769 g, 2.69 mmol) with trimethylsilyl chloride (0.3 mL, 2.69 mmol) in acetonitrile (10 mL) and recrystallization from a mixed solvent (14 mL) of acetonitrile and ether (1 : 6), gave 0.382 g (41%) of rubidium 2-methoxybenzenecarbotelluroate (**2f**) as reddish orange plates: IR (Nujol) 2926, 2856, 1573, 1523 (C=O), 1459, 1278, 1229, 1186, 1118, 1045, 1009, 877, 755, 656, 614, 540 cm^{-1}; ^{1}H NMR (CD_3OD) $\delta=3.78$ (3H, s, CH_3O), 6.89—7.73 (4H, m, Ar); ^{13}C NMR (CD_3OD) $\delta=56.4$ (CH_3O), 113.0, 120.4, 130.8, 130.9, 145.9, 152.3 (Ar), 208.6 (C=O); ^{125}Te NMR (CD_3OD, standard Me_2Te) $\delta=435.2$. Found: C, 27.88; H, 2.11%. Calcd for $C_8H_7O_2RbTe$: C, 27.59; H, 2.03%.

Rubidium 4-Methoxybenzenecarbotelluroate (2g). Similarly to **2c**, the reaction of rubidium fluoride (0.670 g, 6.42 mmol) with *O*-trimethylsilyl 4-methoxybenzenecarbotelluroate (**1g**),[31] freshly prepared from sodium 4-methoxybenzenecarbotelluroate (0.919 g, 3.21 mmol) with trimethylsilyl chloride (0.35 mL, 3.21 mmol) in acetonitrile (10 mL) and recrystallization from a mixed solvent (6 mL) of acetonitrile and ether (1 : 1), gave 0.683 g (61%) of rubidium 4-methoxybenzenecarbotelluroate (**2g**) as orange plates: IR (Nujol) 2959, 2901, 1585, 1563, 1547 (C=O), 1497, 1462, 1377, 1311, 1250, 1177, 1156, 1107, 1020, 880, 841, 644, 614 cm^{-1}; ^{1}H NMR (CD_3OD) $\delta=3.79$ (3H, s, CH_3O), 6.81 (2H, d, $J=8.8$ Hz, Ar), 8.05 (2H, d, $J=8.8$ Hz, Ar); ^{13}C NMR (CD_3OD) $\delta=56.0$ (CH_3O), 113.1, 131.9, 144.1, 163.9 (Ar), 205.9 (C=O); ^{125}Te NMR (CD_3OD, standard Me_2Te) $\delta=184.3$. Found: C, 27.47; H, 1.91%. Calcd for $C_8H_7O_2RbTe$: C, 27.59; H, 2.03%.

Rubidium 4-Chlorobenzenecarbotelluroate (2h). Similarly to **2c**, the reaction of rubidium fluoride (0.973 g, 9.32 mmol) with *O*-trimethylsilyl 4-chlorobenzenecarbotelluroate (**1h**) [λ 728 nm (the n–π^* transitions of C=Te)], freshly prepared from sodium 4-chlorobenzenecarbotelluroate (1.353 g, 4.66 mmol) with trimethylsilyl chloride (0.51 mL, 4.66 mmol) in acetonitrile (10 mL) and recrystallization from a mixed solvent (20 mL) of acetonitrile and ether (1 : 3), gave 0.746 g (45%) of rubidium 4-chlorobenzenecarbotelluroate (**2h**) as reddish orange plates: IR (Nujol) 2920, 1571, 1541 (C=O), 1467, 1378, 1278, 1194, 1154, 1099, 1085, 1010, 874, 833, 725, 595, 552, 466 cm^{-1}; ^{1}H NMR (CD_3OD) $\delta=7.29$ (d, $J=8.0$ Hz, Ar), 8.03 (d, $J=8.0$ Hz, Ar); ^{13}C NMR (CD_3OD) $\delta=128.0$, 130.9, 138.4, 149.6 (Ar), 206.7 (C=O); ^{125}Te NMR (CD_3OD, standard Me_2Te) $\delta=247.6$. Found: C, 23.54; H, 1.09%. Calcd for $C_7H_4ClORbTe$: C, 23.84; H, 1.14%.

Cesium Telluroacetate (3a). Similarly to **3c**, the reaction of cesium fluoride (0.935 g, 6.16 mmol) with *O*-trimethylsilyl telluroacetate (**1a**),[29] freshly prepared from sodium telluroacetate (0.597 g, 3.08 mmol) with trimethylsilyl chloride (0.34 mL, 3.08 mmol) in acetonitrile (10 mL), gave 0.399 g (43%) of cesium telluroacetate (**3a**) as a yellow microcrystalline solid: IR (Nujol) 2975, 1574 (C=O), 1455, 1377, 1334, 1080, 924, 722, 570 cm^{-1}; ^{1}H NMR (CD_3OD) $\delta=2.63$ (s, CH_3); ^{13}C NMR (CD_3OD) $\delta=55.5$ (CH_3), 207.2 (C=O); ^{125}Te NMR (CD_3OD, standard Me_2Te) $\delta=286.9$.

Cesium 2,2-Dimethylpropanetelluroate (3b): Similarly to **3c**, the reaction of cesium fluoride (0.996 g, 6.56 mmol) with *O*-trimethylsilyl 2,2-dimethylpropanetelluoroate (**1b**)[30] [λ 624 nm (the n–π^* transitions of C=Te)], freshly prepared from sodium 2,2-dimethylpropanetelluroate (0.774 g, 3.28 mmol) with trimethylsilyl chloride (0.36 mL, 3.28 mmol) in acetonitrile (10 mL), gave 0.498 g (44%) of cesium 2,2-dimethylpropanetelluroate (**3b**) as a yellow microcrystalline solid: IR (Nujol) 2967, 2863, 1614, 1567 (C=O), 1480, 1457, 1404, 1380, 1355, 1221, 1028, 891, 792, 595, 530 cm^{-1}; ^{1}H NMR (CD_3OD) $\delta=1.08$ (s, CH_3C); ^{13}C NMR (CD_3OD) $\delta=29.0$ ($\underline{C}H_3C$); 55.7 ($CH_3\underline{C}$), 223.1 (C=O); ^{125}Te NMR (CD_3OD, standard Me_2Te) $\delta=80.7$.

Cesium Benzenecarbotelluroate (3c). To a solution of freshly prepared sodium benzenecarbotelluroate[4b)] (0.850 g, 3.32 mmol) in acetonitrile (10 mL), trimethylsilyl chloride (0.36 mL, 3.32 mmol) was added at −10 °C, followed by stirring at the same temperature for 10 min. The color changed from deep red to deep green, indicating the formation of $PhCTeOSiMe_3$ (**1c**) [λ 712 nm (the n–π^* transitions of C=Te)]. Cesium fluoride (1.008 g, 6.64 mmol) was added and stirred at this temperature for 30 min (The color rapidly changed from deep green to deep red). The excesses of CsF and black tellurium were filtered out. Evaporation of the solvent in vacuo, and washing with diethyl ether (5 mL) gave 0.679 g (56% as **3c**) of a dark red solid. Recrystallization from a mixed solvent (5 mL) of acetonitrile and diethyl ether (4 : 1) at 20 °C yielded 0.584 g (48%) of **3c** as orange plates: IR (Nujol) 2926, 2855, 1582, 1555 (C=O), 1463, 1377, 1188, 1155, 1067, 871, 760, 690, 667 cm^{-1}; ^{1}H NMR (CD_3OD) $\delta=7.29$—8.02 (m, Ar); ^{13}C NMR (CD_3OD) $\delta=128.3$, 129.4, 132.2, 151.4 (Ar), 208.6 (C=O); ^{125}Te NMR (CD_3OD, standard Me_2Te) $\delta=254.4$. Found: C, 22.78; H, 1.25%. Calcd for C_7H_5CsOTe: C, 23.00; H, 1.38%.

Cesium 2-Methylbenzenecarbotelluroate (3d). Similarly to **3c**, the reaction of cesium fluoride (0.990 g, 6.52 mmol) with *O*-trimethylsilyl 2-methylbenzenecarbotelluroate (**1d**) [λ 694 nm (the n–π^* transitions of C=Te)], freshly prepared from sodium 2-methylbenzenecarbotelluroate (0.884 g, 3.26 mmol) with trimethylsilyl chloride (0.36 mL, 3.26 mmol) in acetonitrile (10 mL) and recrystallization from a mixed solvent (8 mL) of acetonitrile and ether (1 : 7), gave 0.613 g (50%) of cesium 2-methylbenzenecarbotelluroate (**3d**) as pale orange plates: IR (Nujol) 2981, 2835, 1576, 1557 (C=O), 1455, 1376, 1180, 1112, 880, 854, 775, 757, 714, 665, 610, 489 cm^{-1}; ^{1}H NMR (CD$_3$OD) δ=2.31 (3H, s, CH$_3$), 7.02—7.67 (4H, m, Ar); ^{13}C NMR (CD$_3$OD) δ=20.0 (CH$_3$), 125.5, 128.7, 129.1, 130.0, 131.3, 156.2 (Ar), 212.7 (C=O); ^{125}Te NMR (CD$_3$OD, standard Me$_2$Te) δ=419.7. Found: C, 25.58; H, 2.09%. Calcd for C$_8$H$_7$CsOTe: C, 25.31; H, 1.86%.

Cesium 4-Methylbenzenecarbotelluroate (3e). Similarly to **3c**, the reaction of cesium fluoride (0.879 g, 5.46 mmol) with *O*-trimethylsilyl 4-methylbenzenecarbotelluroate (**1e**)[7)] [λ 700 nm (the n–π^* transitions of C=Te)], freshly prepared from sodium 4-methylbenzenecarbotelluroate (0.738 g, 2.73 mmol) with trimethylsilyl chloride (0.3 mL, 2.73 mmol) in acetonitrile (10 mL) and recrystallization from a mixed solvent (9 mL) of acetonitrile and ether (7 : 2), gave 0.559 g (54%) of cesium 4-methylbenzenecarbotelluroate (**3e**) as orange plates: IR (Nujol) 2982, 2833, 1595, 1574, 1548 (C=O), 1470, 1378, 1157, 878, 820, 773, 723, 613 cm^{-1}; ^{1}H NMR (CD$_3$OD) δ=2.28 (3H, s, CH$_3$), 7.09 (2H, d, J=8.1 Hz, Ar), 7.92 (2H, d, J=8.1 Hz, Ar); ^{13}C NMR (CD$_3$OD) δ=21.4 (CH$_3$), 128.8, 129.8, 142.8, 148.9 (Ar), 207.8 (C=O); ^{125}Te NMR (CD$_3$OD, standard Me$_2$Te) δ=222.3. Found: C, 25.12; H, 1.88%. Calcd for C$_8$H$_7$CsOTe: C, 25.31; H, 1.86%.

Cesium 2-Methoxybenzenecarbotelluroate (3f). Similarly to **3c**, the reaction of cesium fluoride (1.245 g, 8.20 mmol) with *O*-trimethylsilyl 2-methoxybenzenecarbotelluroate (**1f**) [λ 670 nm (the n–π^* transitions of C=Te)], freshly prepared from sodium 2-methoxybenzenecarbotelluroate (1.172 g, 4.10 mmol) with trimethylsilyl chloride (0.45 mL, 4.10 mmol) in acetonitrile (10 mL) and recrystallization from a mixed solvent (15 mL) of acetonitrile and ether (1 : 2), gave 0.764 g (47%) of cesium 2-methoxybenzenecarbotelluroate (**3f**) as yellow plates: IR (Nujol) 2930, 2833, 1591, 1548 (C=O), 1461, 1433, 1234, 1184, 1111, 1044, 1017, 877, 841, 778, 737, 650, 616, 539 cm^{-1}; ^{1}H NMR (CD$_3$OD) δ=3.77 (3H, s, CH$_3$O), 6.84—7.69 (4H, m, Ar); ^{13}C NMR (CD$_3$OD) δ=56.3 (CH$_3$O), 113.0, 120.4, 130.5, 130.9, 146.1, 152.2 (Ar), 208.6 (C=O); ^{125}Te NMR (CD$_3$OD, standard Me$_2$Te) δ=462.5. Found: C, 24.20; H, 1.96%. Calcd for C$_8$H$_7$CsO$_2$Te: C, 24.29; H, 1.78%.

Cesium 4-Methoxybenzenecarbotelluroate (3g). Similarly to **3c**, the reaction of cesium fluoride (1.236 g, 8.14 mmol) with *O*-trimethylsilyl 4-methoxybenzenecarbotelluroate (**1g**),[31)] freshly prepared from sodium 4-methoxybenzenecarbotelluroate (1.162 g, 4.07 mmol) with trimethylsilyl chloride (0.45 mL, 4.07 mmol) in acetonitrile (10 mL) and recrystallization from a mixed solvent (10 mL) of acetonitrile and ether (1 : 1), gave 0.950 g (59%) of cesium 4-methoxybenzenecarbotelluroate (**3g**) as orange plates: IR (Nujol) 2979, 2883, 2835, 1599, 1577, 1545 (C=O), 1453, 1377, 1250, 1154, 1015, 874, 826, 778, 646, 615, 599, 492 cm^{-1}; ^{1}H NMR (CD$_3$OD) δ=3.78 (3H, s, CH$_3$O), 6.81 (2H, d, J=8.8 Hz, Ar), 8.04 (2H, d, J=8.8 Hz, Ar); ^{13}C NMR (CD$_3$OD) δ=56.0 (CH$_3$O), 113.2, 132.0, 144.4, 164.0 (Ar), 205.8 (C=O); ^{125}Te NMR (CD$_3$OD, standard Me$_2$Te) δ= 197.5. Found: C, 24.08; H, 1.91%. Calcd for C$_8$H$_7$CsO$_2$Te: C, 24.29; H, 1.78%.

Cesium 4-Chlorobenzenecarbotelluroate (3h). Similarly to **3c**, the reaction of cesium fluoride (0.656 g, 4.32 mmol) with *O*-trimethylsilyl 4-chlorobenzenecarbotelluroate (**1h**) [λ 728 nm (the n–π^* transitions of C=Te)], freshly prepared from sodium 4-chlorobenzenecarbotelluroate (0.627 g, 2.16 mmol) with trimethylsilyl chloride (0.24 mL, 2.16 mmol) in acetonitrile (10 mL) and recrystallization from a mixed solvent (10 mL) of acetonitrile and ether (1 : 1), gave 0.519 g (61%) of cesium 4-chlorobenzenecarbotelluroate (**3h**) as orange plates: IR (Nujol) 2922, 2855, 1571, 1546 (C=O), 1463, 1377, 1196, 1156, 1098, 1010, 877, 835, 552, 467 cm^{-1}; ^{1}H NMR (CD$_3$OD) δ=7.29 (d, J=8.8 Hz, Ar), 8.00 (d, J=8.8 Hz, Ar); ^{13}C NMR (CD$_3$OD) δ=128.1, 130.9, 138.4, 150.0 (Ar), 206.6 (C=O); ^{125}Te NMR (CD$_3$OD, standard Me$_2$Te) δ=287.8. Found: C, 20.86; H, 1.27%. Calcd for C$_7$H$_4$ClCsOTe: C, 21.02; H, 1.01%.

Reaction of Rubidium Benzenecarbotelluroate (2c) with Iodomethane. To rubidium benzenecarbotelluroate (**2c**) (1.024 g, 3.22 mmol), iodomethane (5 mL, 80 mmol) was added at −20 °C, followed by stirring at the same temperature for 2 h. Separation of the resulting precipitates by filtration, and evaporation of the iodomethane in vacuo gave 0.585 g (73%) of *Te*-methyl benzenecarbotelluroate (**6c**) as an orange liquid. The IR spectrum was exactly consistent with that of the authentic sample prepared from the reaction with sodium benzenecarbotelluroate with iodomethane. (**6c**): IR (Neat) 2926, 1660 (C=O), 1580, 1446, 1261, 1200, 1170, 1026, 868, 800, 762, 685, 666, 596 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.24 (3H, s, CH$_3$), 7.37—7.85 (5H, m, Ar); ^{13}C NMR (CDCl$_3$) δ=13.9 (CH$_3$, satellite $^1J_{\text{Te–C}}$=157 Hz), 126.6, 128.8, 133.5, 142.7 (Ar), 195.5 (C=O); ^{125}Te NMR (CDCl$_3$, standard Me$_2$Te) δ=613.7.

Reaction of Cesium Benzenecarbotelluroate (2c) with Iodomethane. Under the same conditions, the reaction of cesium benzenecarbotelluroate (**3c**) (1.170 g, 3.20 mmol) with iodomethane (5 mL, 80 mmol) gave 0.560 g (71%) of *Te*-methyl benzenecarbotelluroate (**6c**).

Methylene Bis(4-methoxybenzenecarbotelluroate) (7). To a suspension of cesium 4-methoxybenzenecarbotelluroate (**3g**) (0.311 g, 0.78 mmol) in dichloromethane (10 mL), dibenzo-24-crown-8 (0.352 g, 0.78 mmol) was added at 23 °C, followed by stirring at the same temperature for 15 min. (The color of the solution rapidly changed to yellow.) Separation of the resulting precipitates by filtration, and evaporation of the solvent in vacuo gave a yellow solid. Recrystallization from a mixed solvent of dichloromethane and hexane (1 : 4) at 23 °C yielded 0.290 g (69%) of methylene bis(4-methoxybenzenecarbotelluroate) (**7**) as yellow needles: mp 146—149 °C; IR (KBr) 3019, 2985, 1667 (C=O), 1636 (C=O), 1597, 1572, 1502, 1418, 1262, 1210, 1168, 1114, 1068, 1023, 878, 834, 647, 593 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=3.86 (6H, s, CH$_3$O), 4.05 (2H, s, satellite $^2J_{\text{Te–H}}$=31 Hz, CH$_2$), 6.92 (4H, d, J=8.8 Hz, Ar) 7.69 (4H, d, J=8.8 Hz, Ar); ^{13}C NMR (CDCl$_3$) δ=−33.1 (CH$_2$), 55.7 (CH$_3$O) 114.2, 129.3, 135.9, 164.3 (Ar), 195.8 (C=O); ^{125}Te NMR (CDCl$_3$) δ=929.6 (t, $^2J_{\text{Te–H}}$=31 Hz). Found: C, 37.58; H, 2.99%. Calcd for $C_{17}H_{16}O_4Te_2$: C, 37.85; H, 2.99%.

Tetramethylammonium 2-Methoxybenzenecarbotelluroate (8). To a solution of cesium 2-methoxybenzenecarbotelluroate (**3f**) (1.341 g, 3.39 mmol) in acetonitrile (20 mL), tetramethylammonium chloride (0.369 g, 3.39 mmol) was added at 25 °C, followed by stirring at the same temperature for 5 h. Separation of the resulting precipitates by filtration, evaporation of the solvent in vacuo, and washing of the residue with diethyl ether (10 mL) gave 0.885 g (77%) of tetramethylammonium 2-methoxybenzenecarbotelluroate (**8**) as yellow microcrystalline solids: IR (Nujol) 2938, 1575 (C=O), 1464, 1378, 1297, 1271, 1233, 1180, 1104, 1040, 1022, 946, 876, 846, 764, 643, 536 cm^{-1}; ^{1}H NMR (CD_3OD) $\delta=3.18$ (12H, s, NCH_3), 3.75 (3H, s, CH_3O), 6.83—7.65 (4H, m, Ar); ^{13}C NMR (CD_3OD) $\delta=56.1$ (CH_3O), 56.2 (t, $^1J_{C-N}=4.1$ Hz, NCH_3), 112.7, 120.2, 130.2, 130.7, 146.1, 152.3 (Ar), 207.3 (C=O); ^{125}Te NMR (CD_3OD, standard Me_2Te) $\delta=443.4$.

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31) 4-$MeOC_6H_4CTeOSiMe_3$ (**1g**): ^{1}H NMR (270 MHz, $CDCl_3$) $\delta=0.62$ (9H, s, CH_3Si), 3.79 (3H, s, CH_3O), 6.68 (2H, d, $J=9.0$ Hz, Ar), 8.16 (2H, d, $J=9.0$ Hz, Ar); ^{13}C NMR (67.9 MHz, $CDCl_3$) $\delta=1.19$ (CH_3Si), 55.6 (CH_3O), 113.7, 132.5, 146.3, 164.7 (Ar), 221.6 (C=Te); ^{125}Te NMR (85.3 MHz, $CDCl_3$, standard Me_2Te) $\delta=1303$ (C=Te); UV/vis ($CHCl_3$, 25 °C) λ 682 nm (The ^{13}C and ^{125}Te NMR spectra of only $ArCTeOSiMe_3$ have been observed).