A Facile Preparation of Cesium Tellurocarboxylates. The First X-Ray Structural Analysis of a Tellurocarboxylic Acid Alkali Metal Salt

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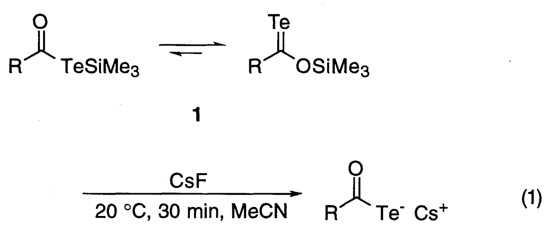
Crystalline cesium tellurocarboxylates have been isolated from the reaction of *O*-trimethylsilyl tellurocarboxylates with cesium fluoride and characterized by X-ray crystallographic analysis which showed a C–Te single bond (2.107 Å) and the possibility of localization of the negative charge on the Te atom.

Over the last two decades much attention has been paid to the chemistry of chalcogenocarboxylic acid derivatives.[1] There are formally 15 families of chalcogenocarboxylic acid alkali metal salts. Though they are important classes of compounds synthetically and spectroscopically, their synthesis and isolation have been limited to only thio- (RCOSM),[2a] seleno- (RCOSeM)[2b] and dithiocarboxylic acid salts (RCSSM)[2c] because of the difficulties encountered in their synthesis and purification.[2] We report herein the isolation and the first characterization of tellurocarboxylic acid alkali metal salts[3] by X-ray diffractions.

The synthesis and isolation of the cesium tellurocarboxylates **2** were achieved by the reaction of the corresponding tellurocarboxylic acid *O*-trimethylsilyl esters[4] **1** with cesium fluoride.[5] The reaction conditions shown in Eq. 1 appear to be preferred. Thus, a solution of *O*-trimethylsilyl 4-methylbenzenecarbotelluroate **1a**[6] freshly prepared by the reaction of sodium 4-methylbenzenecarbotelluroate[3b] with trimethylsilyl chloride in acetonitrile was added to an excess of cesium fluoride at 0 °C and stirred at 20 °C for 30 min. The color rapidly changed from deep green to deep red. Remaining of CsF and a trace of deposited black tellurium were filtered out, and the solvent was evaporated in vacuo. Recrystallization of the residual solid from a mixed solvent of acetonitrile and diethyl ether afforded cesium 4-methylbenzenecarbotelluroate **2a** in 54 % yield as dark red crystals.[7] A similar reaction of *O*-trimethylsilyl 2-methoxybenzenecarbotelluroate **1b** afforded 47 % of cesium 2-methoxybenzenecarbotelluroate **2b**.[8]



1

(1)

2a: R= 4-MeC$_6$H$_4$
2b: R= 2-MeOC$_6$H$_4$

The obtained cesium salts **2** are relatively stable toward heat and moisture, and under argon atmosphere **2** can be stored at 20 °C for at least one week without affecting analytical and spectroscopic data. However, **2** is highly sensitive toward oxygen and quickly decomposes in air with liberation of black tellurium.

The structure of **2b** determined by X-ray diffraction analysis is shown in Fig. 1.[9] The C=O bond length is 1.227(6) Å which is close to those of common carboxylic acid esters. The bond length between the carbonyl carbon and tellurium atom [2.107(5) Å] is indicative of a carbon–tellurium single bond,[10] while the Te–Cs bond length [3.901(1) Å] is close to the sum of the radii of Te and Cs ions.[11] The C–Te–Cs angle is very narrow (69.4 °), and the cesium ion is located out of plane of the tellurocarboxyl group by 1.24 Å [Cs(1)–Te(1)–C(7)–C(1): 162.0(4) °]. In addition, the distance between the carbonyl oxygen and cesium cation is 3.096(4) Å, suggesting the possibility of an intramolecular coordination of the oxygen atom to the metal. These results together with the observation of the ^{125}Te signals (δ 222.3 for **2a** and δ 462.5 for **2b**)[12] in an upfield region indicate that the negative charge of the salts **2** mainly resides on the Te atom.

We are now attempting to synthesize not only a variety of main-group and transition metal derivatives but also extremely labile tellurocarboxylic acids.

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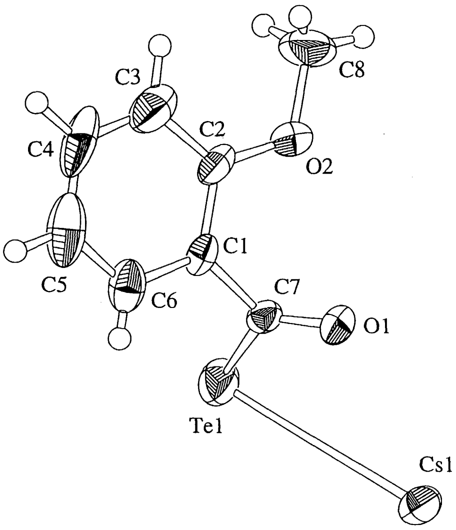

Figure 1. ORTEP drawing of **2b**. Selected bond distances (Å) and angles (deg): Cs(1)–Te(1) 3.901(1), O(1)–C(7) 1.227(6), Te(1)–C(7) 2.107(5), O(1)–C(7)–Te(1) 125.6(4), C(1)–C(7)–Te(1) 114.8(4), O(1)–C(7)–C(1) 119.6(5), C(7)–Te(1)–Cs(1) 69.4(1), O(1)–C(7)–C(1)–C(6) 112.8(6), Cs(1)–Te(1)–C(7)–O(1) 19.9(4), Cs(1)–Te(1)–C(7)–C(1) 162.0(4)

References and Notes

1 (a) K. A. Jensen, H. Mygind, and P. H. Nielsen, in *Organic Selenium Compounds: Their Chemistry and Biology* (Eds. D. L. Klayman and W. H. H. Günther), Wiley-Interscience, New York, **1973**, p. 277; (b) S. Scheithauer and R. Mayer, in *Topics in Sulfur Chemistry,* Vol. 4 (Ed. A. Senning), George Thieme Verlag, Stuttgart, **1979**; (c) S. Kato, T. Murai, and M. Ishida, *Org. Prep. Proceds. Int.,* **18**, 369 (1986); (d) A. Ogawa and N. Sonoda, in *Comprehensive Organic Synthesis* (Ed. B. M. Trost), Pergamon Press, Oxford, **1991**: Vol. 6, p. 461; (e) S. Kato and T. Murai, in *Supplement B*: *The Chemistry of Acid derivatives*, Vol. 2 (Ed. S. Patai), John Wiley & Sons, New York, **1992**, pp. 803–847.

2 (a) S. Kato, M. Oguri, and M. Ishida, *Z. Naturforsch.*, **38b**, 1585 (1983) and references therein. (b) Y. Kawahara, S. Kato, T. Kanda, T. Murai, and H. Ishihara, *J. Chem. Soc., Chem. Commun.*, **1993**, 277 and references therein. (c) R. Mayer and S. Scheithauer, in *Houben-Weyl Methoden der Organischen Chemie*, E5, Teil. 2 (Ed. J. Falbe), Georg Thieme Verlag, Stuttgart, **1985**, p. 891.

3 The following alkali metal tellurocarboxylates have been prepared without purification by recrystallization. RCOTeLi: (a) S. Kato, H. Sasaki, and M. Yagihara, *Phosphorus, Sulfur, and Silicon*, **67**, 27 (1992). RCOTeNa: (b) From RCOCl + Na$_2$Te [T. Kanda, S. Nakaiida, T. Murai, and S. Kato, *Tetrahedron Lett.*, **30**, 1829 (1989)]. (c) From (RCO)$_2$Te + EtONa [S. Kato, H. Kageyama, T. Kanda, T. Murai, and T. Kawamura, *Tetrahedron Lett.*, **31**, 3587 (1990)]. RCOTeK: (d) T. Kakigano, T. Kanda, M. Ishida, and S. Kato, *Chem. Lett.*, **1987**, 475.

4 du Mont et al. have reported the preparation of *Te*-trimethylsilyl alkanecarbotelluroate (RCOTeSiMe$_3$): From RCOCl + (Me$_3$Si)$_2$Te [T. Severengiz, W. W. du Mont, D. Lenior, and H. Voss, *Angew. Chem., Int. Ed. Engl.*, **24**, 1041 (1985)]. The equilibrium between RCOTeSiR'$_3$ and RCTeOSiR'$_3$ has been found (T. Severengiz and W. W. du Mont, *J. Chem. Soc., Chem. Commun.*, **1987**, 820) and ref. 3c.

5 The methodologies shown in Ref. 3 can not be applied to the preparation of cesium salts **2** because of the difficulty of the synthesis of cesium telluride and alkoxides. Furthermore, the salt-exchange reaction which has been employed for the preparation of sulfur analogues[2a] is also unsuitable owing to the extreme instability of tellurocarboxylic acids themselves.

6 4-MeC$_6$H$_4$CTeOSiMe$_3$ (**1a**): ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.66 (s, 9H, CH$_3$Si), 2.07 (s, 3H, CH$_3$Ar), 7.01 (d, *J* = 8.8 Hz, 2H, Ar), 8.08 (d, *J* = 8.8 Hz, 2H, Ar); ^{13}C NMR (67.9 MHz, CDCl$_3$) δ 1.14 (CH$_3$Si), 22.1 (CH$_3$Ar), 129.2, 130.0, 144.2, 150.8 (Ar), 223.7 (C=O); ^{125}Te NMR (85.3 MHz, CDCl$_3$, standard Me$_2$Te) δ 1438 (C=Te); UV/VIS (CHCl$_3$, 25 °C) λ 700 nm (In the ^{13}C and ^{125}Te NMR spectra, only the signals of ArCTeOSiMe$_3$ have been observed).

7 **2a** as orange plates: IR (nujol) ν 2982, 2833, 1595, 1574, 1548 (C=O), 1470, 1378, 1157, 878, 820, 773, 723, 613 cm^{-1}; ^{1}H NMR (270 MHz, CD$_3$OD) δ 2.28 (s, 3H, CH$_3$), 7.09 (d, *J* = 8.1 Hz, 2H, Ar), 7.92 (d, *J* = 8.1 Hz, 2H, Ar); ^{13}C NMR (67.9 MHz, CD$_3$OD) δ 21.4 (CH$_3$), 128.8, 129.8, 142.8, 148.9 (Ar), 207.8 (C=O); ^{125}Te NMR (85.3 MHz, CD$_3$OD, standard Me$_2$Te) δ 222.3; Anal. Calcd for C$_8$H$_7$CsOTe: C, 25.31; H, 1.86. Found: C, 25.12; H, 1.88.

8 **2b** as orange plates: IR (nujol) ν 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 (270 MHz, CD$_3$OD) δ 3.77 (s, 3H, CH$_3$O), 6.84-7.69 (m, 4H, Ar); ^{13}C NMR (67.9 MHz, 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 (85.3 MHz, CD$_3$OD, standard Me$_2$Te) δ 462.5; Anal. Calcd for C$_8$H$_7$CsO$_2$Te: C, 24.29; H, 1.78. Found: C, 24.20; H, 1.96.

9 Crystal data of **2b**: C$_8$H$_7$CsO$_2$Te, MW = 395.65, monoclinic, space group P2$_1$/n, a = 7.182(2), b = 12.161(5), c = 12.151(3) Å, ß = 92.57(2) °, V = 1060.2(6) Å^3, Z = 4, Dc = 2.479 g/cm^3, μ = 61.5 cm^{-1}, R = 0.036, R$_w$ = 0.028 for 2049 observed reflections [$I > 3.00\sigma(I)$].

10 The C–Te single bonds of 1,2,4-oxatellurazole show 2.105(7) and 2.175(7) Å (M. Minoura, T. Kawashima, and R. Okazaki, *Chem. Lett.*, **1994**, 1691), while that of (CF$_2$Te)$_2$ is 2.191(11) Å (R. Boese, A. Haas, and C. Limberg, *J. Chem. Soc., Chem. Commun.*, **1991**, 1378).

11 (a) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.*, **B25**, 925 (1969). (b) R. D. Shannon, *Acta Crystallogr.*, **A32**, 751 (1976).

12 In general, the ^{77}Se signals of ortho-substituted aromatic selenoesters and selenoic acid alkali metal salts appear in more downfield region than those of para-substituted ones.