Monooxytellurane(IV) Derivatives ([10−Te−4(C3O)]). Syntheses and Molecular Structure of Triaryltelluronium Carboxylate Compounds

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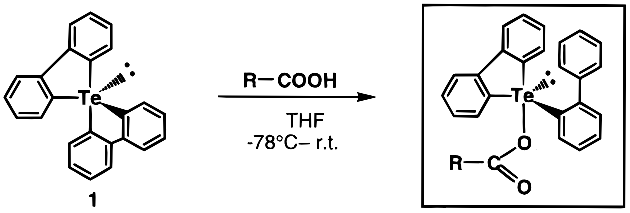
*Summary: Bis(2,2′-biphenylylene)tellurane (**1**) undergoes a ring-opening reaction on treatment with acetic and benzoic acid to afford the triaryltelluronium carboxylate derivatives [10−Te−4(C3O)] (**2**). (2,2′-Biphenylylene)-(2-biphenylyl)benzoyloxytellurane (λ^4-tellane) (**2a**) and (2,2′-biphenylylene)(2-biphenylyl)acetyloxytellurane (λ^4-tellane) (**2b**) were subjected to X-ray crystallographic analysis, which revealed that they crystallize as monomers and dimers, respectively, and that their Te centers have a distorted trigonal-bipyramidal bonding geometry.*

Scheme 1



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2a (R = Ph)
2b (R = CH_3)

Introduction

Organic tellurium carboxylate compounds are one of the oldest known hypervalent organic tellurium species.[1] Although these compounds are relatively stable, only a few have been reported. To date, only two types of compounds have been reported, namely, diorganyltellurium dicarboxylate and monoorganyltellurium tricarboxylate species. The former is very stable and was synthesized by reacting diorganyltellurium dihalides with a silver or sodium carboxylate,[2] a diorganyltelluride with a lead(IV) carboxylate,[3] or a diorganyltelluroxide with a carboxylic anhydride.[4] The structures of bis(*p*-methoxyphenyl)tellurium diacetate and μ-oxo-bis-[diphenyltrifluoroacetoxytellurium]hydrate have been determined by X-ray crystallographic analysis, revealing that the structures involve secondary bonding.[5] More recently, we have reported the preparation of 1,1′-spiro-bis(3*H*-2,1-benzoxatellurole)-3,3′-dione [10−Te−4(C2O2)][6] with five-membered spiro rings, and its molecular structure was determined by X-ray diffraction.[7] In contrast, the latter was synthesized by the reaction of diphenyl ditelluride with lead(IV) tetraacetate.[8] However, this product undergoes rapid hydrolytic decomposition in moist air and could only be characterized by ^{1}H NMR spectroscopy. In 1988, Wieber et al. reported the preparation of some triorganyltelluronium carboxylate compounds obtained by reacting triphenyltelluronium methoxide with carboxylic acid derivatives.[9] However, it remains an open question whether the structures of these species are of the hypervalent type [10−Te−4(C3O)] (λ^4-tellane) or telluronium salt type. Recently, we carried out the reaction of bis(2,2′-biphenylylene)tellurane (**1**)[10] with phenol derivatives in order to investigate the reactivity of telluranes having only carbon ligands, and succeeded in isolating the (2,2′-biphenylylene)(2-biphenyl)phenoxytellurane derivatives [10−Te−4(C3O)] (λ^4-tellane), and determined its structure by X-ray analysis.[11] Now, we have reacted the tellurane (**1**) with carboxylic acid derivatives and obtained both (2,2′-biphenylylene)(2-biphenylyl)benzoyloxytellurane (**2a**) and (2,2′-biphenylylene)(2-biphenylyl)-acetyloxytellurane (**2b**) as stable crystals in quantitative yield, allowing an X-ray analysis in each case (Scheme 1). Here, we describe the isolation and a detailed characterization of (2,2′-biphenylylene)(2-biphenylyl)benzoyloxytellurane and (2,2′-biphenylylene)(2-biphenylyl)-acetyloxytellurane and their first structural determination by X-ray crystallographic analysis.

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(11) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography;* The Kynoch Press: Birmingham, England, 1974, Vol. IV, Table 2.2B.

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Experimental Section

General Methods. All NMR spectra were obtained with a JEOL LMN-EX-270 spectrometer. Mass spectra were taken with a JEOL JMX SX102 mass spectrometer. IR spectra were recorded on a JASCO FT/IR-300F spectrometer. The X-ray crystallographic analysis was performed with a four-circle Enraf-Nonius CAD4-FR automatic diffractometer. Elemental analyses were carried out by the Chemical Analytical Center at the University of Tsukuba. All melting points are uncorrected. Each chemical shift was determined by two-dimensional shift correlation ($^1H-^1H$ and $^{13}C-^1H$ COSY) spectra.

Materials. All solvents and reagents were dried and purified according to standard methods. Bis(2,2′-biphenylylene)tellurane (**1**) was prepared according to ref 10.

Preparation of (2,2′-Biphenylylene)(2-biphenylyl)benzoyloxytellurane (2a). To a solution of tellurane **1** (106 mg, 0.25 mmol) in dry benzene (20 mL), purified benzoic acid (28 mg, 0.26 mmol) was added, and the solution was stirred for 1 h under argon at room temperature. After removal of the solvent, the residue was recrystallized from 3:1 dry benzene: *n*-hexane under argon to give pale yellow crystals (112 mg, 95%): mp 222−223 °C (dec); ^1H NMR (270 MHz, $CDCl_3$, room temperature) δ 7.15 (t, $J = 8.9$ Hz, 1H, 16-ArH), 7.32 (t, $J = 9.2$ Hz, 2H, 5-ArH), 7.33 (t, $J = 8.9$ Hz, 2H, 15-ArH), 7.35 (t, $J = 9.6$ Hz, 2H, 19-ArH), 7.35 (d, $J = 9.3$ Hz, 1H, 11-ArH), 7.38 (d, $J = 8.9$ Hz, 2H, 14-ArH), 7.42 (t, $J = 9.3$ Hz, 1H, 10-ArH), 7.45 (d, $J = 9.2$ Hz, 2H, 3-ArH), 7.49 (t, $J = 9.2$ Hz, 2H, 4-ArH), 7.55 (t, $J = 9.6$ Hz, 1H, 20-ArH), 7.62 (t, $J = 9.3$ Hz, 1H, 9-ArH), 7.81 (d, $J = 9.2$ Hz, 2H, 6-ArH), 7.88 (d, $J = 9.3$ Hz, 1H, 8-ArH), 8.06 (d, $J = 9.6$ Hz, 2H, 18-ArH); ^{13}C NMR (67.8 MHz, $CDCl_3$, room temperature) δ 123.9, 127.6, 129.0, 129.1, 129.3, 129.5, 129.7, 129.7, 130.2, 130.4, 130.5, 131.3, 131.8, 132.0, 134.6, 135.3, 136.2, 141.6, 144.7, 146.0, 172.4; ^{125}Te NMR (85.2 MHz, $CDCl_3$, room temperature) δ 720.2 (relative to Me_2Te); IR (ν, cm^{-1}) 1553 (KBr, ν_{as}(C−O)), 1552 (mull, ν_{as}(C−O)), 1555 ($CHCl_3$, ν_{as}(C−O)), 1359 (KBr, ν_s(C−O)), 1359 (mull, ν_s(C−O)), 1363 ($CHCl_3$, ν_s(C−O)); MS (*m*/*z*) 435 ($M^+ - 121$). Anal. Calcd for $C_{31}H_{22}O_2Te$: C, 67.20; H, 4.00. Found: C, 67.30; H, 3.95.

Preparation of (2,2′-Biphenylylene)(2-biphenylyl)-acetyloxytellurane (2b). To a solution of tellurane **1** (106 mg, 0.25 mmol) in dry benzene (20 mL), purified acetic acid (28 mg, 0.26 mmol) was added, and the solution was stirred for 1 h under argon at room temperature. After removal of the solvent, the residue was recrystallized from 3:1 dry benzene:*n*-hexane under argon to give pale yellow crystals (112 mg, 93%): mp 162−165 °C (dec); ^1H NMR (270 MHz, $CDCl_3$, room temperature) δ 2.02 (s, 3H, Me), 7.14 (t, $J = 9.6$ Hz, 1H, 9-ArH), 7.24 (d, $J = 9.6$ Hz, 1H, 8-ArH), 7.34 (t, $J = 9.5$ Hz, 2H, 5-ArH), 7.34 (t, $J = 9.6$ Hz, 1H, 10-ArH), 7.36 (d, $J = 9.6$ Hz, 1H, 11-ArH), 7.44 (d, $J = 9.5$ Hz, 2H, 3-ArH), 7.50 (t, $J = 9.5$ Hz, 2H, 4-ArH), 7.60 (t, $J = 9.6$ Hz, 1H, 16-ArH), 7.68 (t, $J = 9.6$ Hz, 2H, 15-ArH), 7.81 (d, $J = 9.5$ Hz, 2H, 6-ArH), 7.83 (d, $J = 9.6$ Hz, 2H, 14-ArH); ^{13}C NMR (67.8 MHz, $CDCl_3$, room temperature) δ 24.0, 123.9, 129.1, 129.1, 129.3, 129.6, 129.6, 130.3, 130.4, 131.3, 131.4, 131.8, 134.4, 135.1, 141.5, 144.6, 145.9, 177.8; ^{125}Te NMR (85.2 MHz, $CDCl_3$, room temperature) δ 714.5; IR (ν, cm^{-1}) 1568 (KBr, ν_{as}(C−O)), 1568 (mull, ν_{as}(C−O)), 1557 ($CHCl_3$, ν_{as}(C−O)), 1379 (KBr, ν_s(C−O)), 1374 (mull, ν_s(C−O)), 1388 ($CHCl_3$, ν_s(C−O)); MS (*m*/*z*) 435 ($M^+ - 59$). Anal. Calcd for $C_{26}H_{20}O_2Te$: C, 63.47; H, 4.10. Found: C, 63.80; H, 4.27.

X-ray Crystallographic Analysis of 2a and 2b. Suitable crystals were mounted on top of a glass fiber, and their respective X-ray data were collected using an Enraf-Nonius CAD4-FR four-circle diffractometer employing graphite-monochromated Mo Kα radiation ($\lambda = 0.710$ 73 Å) employing the $\omega/2\theta$ scan technique. The crystallographic details are given in Table 1. Selected bond distances and angles of **2a** and **2b** are given in Table 2. Non-hydrogen atoms were modeled anisotropically using neutral-atom scattering factors. The hydrogen atoms were added to the respective carbon atoms assuming a planar geometry with the C−H distances equal to 1.08 Å, but their positions were not refined. All structures were refined on *F* by full-matrix least-squares techniques. The neutral-atom scattering factors used in the refinements were taken from Cromer and Waber[11] and corrected for anomalous dispersion[12] using the *f* ′ and *f*″ values determined by Creagh and McAuley.[13] The teXsan[14] crystallographic software package was used for the refinement and geometrical calculations and molecular graphics. All calculations were performed on

Table 1. X-ray Crystallographic Data for Diffraction Studies of 2a and 2b

	2a	**2b**
formula	$C_{31}H_{22}O_2Te$	$C_{26}H_{20}O_2Te$
fw	554.11	492.04
cryst syst	triclinic	tetragonal
space group	$P\bar{1}$ (No. 2)	$I4_1/a$ (No. 88)
a, Å	10.590(2)	30.731(1)
b, Å	10.910(2)	
c, Å	11.843(1)	10.189(1)
α, deg	85.54(1)	
β, deg	78.76(1)	
γ, deg	64.35(1)	
V, $Å^3$	1209.8(3)	9622.4(8)
Z	2	16
D_{calcd}, g cm^{-3}	1.521	1.358
F(000)	552	3094
temp, °C	23 ± 1	23 ± 1
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
cryst dimens, mm	0.30 × 0.50 × 0.60	0.80 × 0.80 × 1.00
μ, cm^{-1}	12.56	12.53
scan type	$\omega-2\theta$	$\omega-2\theta$
scan rate, deg/min	2−20	2−20
scan width, deg	$0.8 + 0.520 \tan\theta$	$0.5 + 0.400 \tan\theta$
max 2θ, deg	49.9	49.9
total no. of rflns	4492	4010
no. of unique rflns	4245	3992
no. of params refined	308	262
no. of rflns included	4155 with $F_o^2 > 3.0\sigma(F_o^2)$	3013 with $F_o^2 > 3.0\sigma(F_o^2)$
agreement factors[a]		
R	0.025	0.027
R_w	0.029	0.034

Table 2. Selected Bond Distances (Å) and Angles (deg) of 2a and 2b

compound **2a**	compound **2b**
Te(1)−O(1) = 2.469(3)	Te(1)−O(1) = 2.491(4)
Te(1)−O(2)−3.182(3)	Te(1)−O(2) = 3.181(4)
Te(1)−C(1) = 2.131(3)	Te(1)−O(2)′ = 3.046(4)
Te(1)−C(12) = 2.110(3)	Te(1)−C(1) = 2.152(5)
Te(1)−C(13) = 2.133(3)	Te(1)−C(12) = 2.116(5)
O(1)−C(25) = 1.246(4)	Te(1)−C(13) = 2.146(5)
O(2)−C(25) = 1.232(4)	O(1)−C(25) = 1.250(6)
	O(2)−C(25) = 1.220(6)
O(1)−Te(1)−C(1) = 159.9(1)	O(1)−Te(1)−C(1) = 160.1(2)
O(1)−Te(1)−C(12) = 81.7(1)	O(1)−Te(1)−C(12) = 81.8(2)
O(1)−Te(1)−C(13) = 81.4(1)	O(1)−Te(1)−C(13) = 81.2(2)
C(1)−Te(1)−C(12) = 80.9(1)	C(1)−Te(1)−C(12) = 80.3(2)
C(1)−Te(1)−C(13) = 91.5(1)	C(1)−Te(1)−C(13) = 92.3(2)
C(12)−Te(1)−C(13) = 99.3(1)	C(12)−Te(1)−C(13) = 97.2(2)
Te(1)−O(1)−C(25) = 112.5(2)	Te(1)−O(1)−C(25) = 111.4(3)
Te(1)−O(2)−C(25) = 77.9(2)	O(1)−C(25)−O(2) = 126.0(5)
O(1)−C(25)−O(2) = 125.7(3)	O(2)−Te(1)−O(2)′ = 101.15(9)
	Te(1)−O(2)−Te(1)′ = 78.85(9)
	O(1)−Te(1)−O(2)′ = 105.7(1)
	O(1)−Te(1)−O(2) = 43.6(1)

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(13) Creagh, D. C.; McAuley, W. J. *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Boston, 1992; Table 4.2.6.8, p 219.

(14) teXsan: Crystal Structure Analysis Package, Molecular Structure Corp: The Woodlands, TX, 1985 1992.

an Indy workstation. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre (CCDC No. 101225).

Compound 2a. The unit cell parameters were determined from a least-squares treatment of 25 reflections in the range $12.0° < 2\theta < 21.0°$. The intensities of 4492 reflections measured at 23 °C were corrected for *Lp* effects, absorption (DIFABS,[15] correction range 0.84–1.00), crystal decay (1.0%), and secondary extinction (coefficient = 3.15050×10^{-7}). The structure was solved by direct methods[16] and expanded using difference Fourier syntheses.[17] The final cycle of full-matrix least-squares based on 4155 reflections ($I > 3.0\sigma(I)$) and 308 variable parameters converged with $R = 0.025$ and $R_w = 0.029$. The remaining maximum and minimum electron density features in the final difference Fourier map are equal to 0.78 and −0.47 e/Å^3, respectively.

Compound 2b. A colorless rodlike crystal was used to determine the unit cell from the SET4 setting angles of 25 reflections in the range $12.0° < 2\theta < 21.0°$. The intensities of 4010 reflections measured at 23 ± 1 °C were corrected for *Lp* effects, absorption (DIFABS,[15] correction range 0.92–1.00), crystal decay (2.4%), and secondary extinction (coefficient = 3.15050×10^{-7}). The structure was solved by direct methods[16] and expanded using difference Fourier syntheses.[17] The final cycle of full-matrix least-squares (3013 reflections ($I > 3.0\sigma(I)$); 262 variables) converged with $R = 0.027$ and $R_w = 0.034$. The residual electron density features in the final difference Fourier map are in the range from 0.48 to −0.27 e/Å^3.

Results and Discussion

The tellurane **1** reacted with an equimolar amount of benzoic or acetic acid in dry benzene at room temperature. After removal of the solvent, the corresponding carboxyloxytellurane **2a** or **2b** was isolated as stable, colorless crystals in 95% or 93% yield, respectively. The initial characterization of **2a** and **2b** was carried out by ^{1}H,^{13}C, and ^{125}Te NMR, mass spectroscopy, and elemental analysis.

Generally, the ^{125}Te chemical shifts of triaryloxytellurium compounds in the form of hypervalent and onium salt species are not significantly different.[18] To test whether the structures of **2a** and **2b** were of the hypervalent type, [10–Te–4(C3O)] or the corresponding onium salt, their IR spectra were measured by three different methods (KBr, mull, and $CHCl_3$). IR bond stretches for **2a** and **2b** were observed at 1564 (ν_{as}(C–O)), 1379 cm^{-1} (ν_s(C–O)) and 1553 (ν_{as}(C–O)), 1360 cm^{-1} (ν_s(C–O)) and assigned as the absorptions resulting from the carbon–oxygen bonds in the carboxyl groups. They are comparable to those of the compounds reported as triphenyltelluronium salts by Wieber et al.[9] These results indicate that the benzoic groups have the character of carboxylic anions[19] and that the structures of these compounds are similar in both the solid and solution states. Therefore, these compounds were expected to exist in the form of an onium salt rather than the usual hypervalent type.

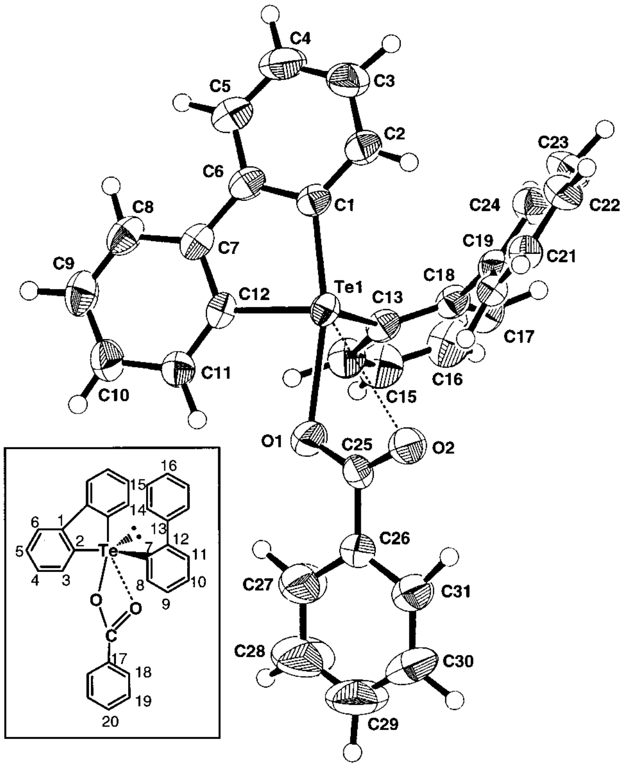

Figure 1. ORTEP (50% probability ellipsoids) drawing of **2a** showing the atom-numbering scheme.

Furthermore, we have succeeded in determining the structures of the products **2a** and **2b** by X-ray crystallographic analysis. The single crystals of **2a** and **2b** were obtained by recrystallization of the respective compound from dry THF.

An ORTEP diagram of a single molecule of **2a** showing the numbering scheme is displayed in Figure 1. The Te(1)–O(1) bond distance of **2a** is 2.469(3) Å which is much longer than that of the Te–O single bond (2.101 Å)[20] but agrees with the apical Te–O bond distance of the 10–Te–4(C3O) species which has an electron-withdrawing substituent on an oxygen atom.[18] The bond angles O(1)–Te(1)–C(1) and C(12)–Te(1)–C(13) of **2a** are 159.9(1)° and 99.3(1)°, respectively. This gives no indication of the bridge, and indeed, the four atoms closest to the tellurium atom, C(1), C(12), C(13), and O(1), together with the supported lone-electron pair appear to provide the distorted, pseudo-trigonal-bipyramidal (ψ-tbp) environment. The configuration of **2a** is very close to that of the tetraphenyl-[21] and bis(2,2′-biphenylylene)tellurane (**1**) and the corresponding oxytelluranes,[18] whose structures have already been determined previously by X-ray crystallographic analysis. Hence, the structure of **2a** is obviously an example of a tellurane [10–Te–4(C3O)] type in which the benzoic oxygen and one Te–C bond of dibenzotellurophene compose the apical bonds. The phenyl rings have

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(15) *DIFABS*: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158. An empirical absorption correction program.

(16) *SIR92*: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1998**, manuscript in preparation.

(17) *DIRDIF94*: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-94 program system*; Technical Report of the Crystallography Laboratory, University of Nijmegen: The Netherlands, 1994.

(18) (a) Sato, S.; Kondo, N.; Furukawa, N. *Organometallics* **1994**, *13*, 3393. (b) Sato, S.; Kondo, N.; Furukawa, N. *Organometallics* **1995**, *14*, 5393.

(19) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric identification of organic compounds*, 5th ed., John Wiley and Sons: New York, 1991. For example, IR signals of ammonium benzoate have been observed at 1550 (ν_{as}(C–O)) and 1385 cm^{-1} (ν_s(C–O)) as the signals of carbon–oxygen bonds in the carboxyl group.

(20) Bergman, J.; Engman, L.; Siden, J. *The chemistry of organic selenium and tellurium compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1986; Vol. 1, p 78 and references therein.

(21) Smith, C. S.; Lee, J.-S.; Titus, D. D.; Ziolo, R. F. *Organometallics* **1982**, *1*, 350.

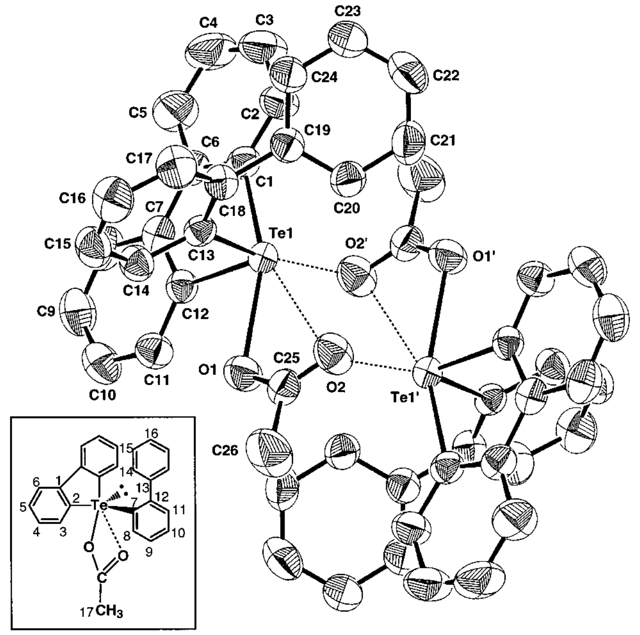

Figure 2. ORTEP (50% probability ellipsoids) drawing of **2b** showing the atom-numbering scheme. For clarity, the hydrogens on the phenyl groups were omitted.

normal geometries (bond lengths 1.349−1.411 Å, bond angles 116.7−122.5°). In the benzoic oxygen ligand configuration, the C(25)−O(1) bond distance of 1.246(4) Å is a little longer than the C(25)−O(2) distance of 1.232(4) Å. However, the COO^- skeleton in **2a** is less asymmetric than that of carboxylate salt analogues and the distances are smaller than the corresponding carbon−oxygen bond distances in the benzoic acid (C−OH = 1.29 Å, C═O = 1.24 Å).[22] The Te(1), C(25), O(1), and O(2) atoms in **2a** are on the same plain because the sum of the angles between these atoms is about 360°. The Te(1)−O(2) distance, 3.182(3) Å, is between the sum of the 1,3-intramolecular nonbonded radii (2.87 Å) and van der Waals radii (3.60 Å) in the Te−O bond.[20] Therefore, this interaction can be regarded as an intramolecular secondary bond. In the unit cell, the closest intermolecular Te−O approach is 6.832 Å, and thus, **2a** packs as monomeric molecules independent of their neighbors.

An ORTEP diagram of the single molecule of **2b** showing the numbering scheme is illustrated in Figure 2. The Te(1)−O(1) bond distance in **2b** is 2.491(4) Å, and the bond angles of O(1)−Te(1)−C(1) and C(12)−Te(1)−C(13) of **2b** are 160.1(2)° and 97.2(2)°, respectively. The configuration around the central tellurium atom is that of a distorted trigonal bipyramid, and the corresponding bond distances and angles of **2b** are similar to those of **2a** in the intramolecule domain. However, in the crystal lattice, **2b** exists as a dimer as a result of the secondary bond formation between the tellurium and an oxygen of the acetyl group of two neighboring molecules. The closest intermolecular approach, Te(1)−O(2)′, is 3.046(4) Å. This Te(1)−O(2)′ distance is a little smaller than the intramolecular Te(1)−O(2) bond distance, 3.181(4) Å. In addition, the Te(1), Te(1)′, O(2), and O(2)′ atoms in **2b** form a four-membered ring and are located on the same plane. In the discrete dimeric species, the two Te atoms are situated in an approximately distorted octahedral coordination environment.

Thus, differences between the structures of **2a** and **2b** may be due to steric factors arising from the size of the substituent influencing the carboxyl group and the influence of crystal packing forces. Such behavior has been reported for the triphenyltelluronium methylxanthate derivatives by Singh et al.[23] They have suggested that the structural difference between triphenyltelluronium methylxanthate (as a dimer form) and isobutylxanthate depended on the steric influence of the alkyl group of the xanthate system.

The compounds **2a** and **2b** have typical tellurane structures having not only asymmetric three-center four-electron bonds but also secondary bonding. The IR spectra results of **2a** and **2b** described above can explain the large polarizability of the hypervalent bond. The present results provide a new procedure for the synthesis of oxytellurane (λ^4-tellane).

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Supporting Information Available: Text giving the experimental data and tables of crystal data, positional parameters, thermal parameters, root mean-square amplitudes, and bond distances and angles (23 pages). Ordering information is given on any current masthead page.

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