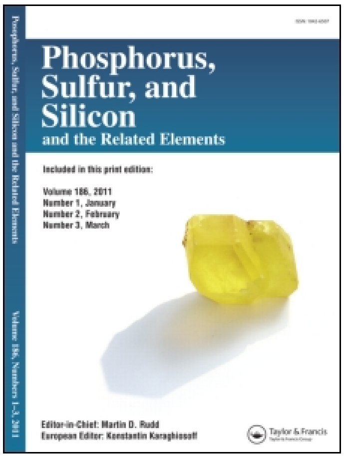

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# SYNTHESIS AND CHARACTERIZATION OF NEW SPIROOXYTELLURANE [10-Te-4(C3O)] HAVING $SO_3$ UNIT

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***Bis(2,2′-biphenylylene)tellurane 1 reacted with an equivalent of sulfuryl chloride to give a new spirooxytellurane 2 having $SO_3$ unit at the apical site as a stable colorless crystal together with bis(2,2′-biphenylylene)dichloropertellurane 3. The structure of spirooxytellurane 2 was determined by X-ray crystallographic analysis, revealing that it has a distorted trigonal bipyramidal (TBP) bonding geometry.***

**Keywords** Hypercoordinate; $SO_3$ unit; spirooxytellurane; trigonal bipyramidal structure; X-ray crystallographic analysis

## INTRODUCTION

Studies on hypercoordinated organo-chalcogen compounds have attracted attention because they seem to open a new frontier in organic chemistry, which is based upon the extraordinary unusual chemical characters compared with those of the general organic compounds in which a carbon atom plays a pivotal role. A number of stable hypercoordinated chalcogen compounds (chalcogenuranes and perchalcogenuranes) having strong electron-withdrawing ligands have been synthesized, and their chemistry has been studied in depth.[1] Especially, the hypercoordinated tellurium compounds (telluranes and pertelluranes) have been well reported because they are the most stable among the corresponding chalcogen compounds. In general, the hypercoordinated chalcogen compounds having only carbon ligands have rarely been reported regarding their syntheses, reactivities, and structures.[1] The major problem is their poor stability due to the self-decomposition by the ligand coupling reaction and the hydrolysis by a small amount of water contained in the air and solvent. However, the tetraaryl chalcogen compounds bearing two biphenylylene ligands

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Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

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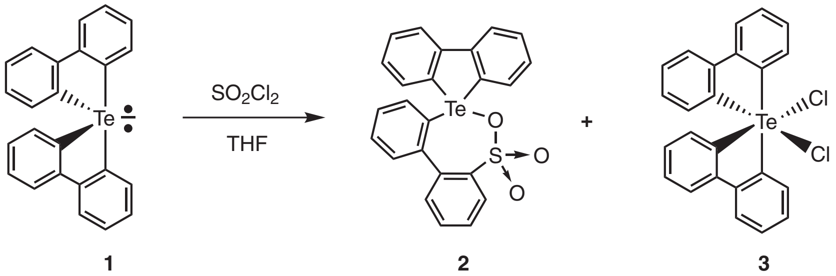
can be isolated as metastable products, and have been explored not only by the determination of structures but also the reactivities for nuclephilic, protonating, and halogenating reagents.[2] Previously, we reported that treatment of bis(2,2′-biphenylylene)tellurane **1**[3] with sulfuryl chloride ($SO_2Cl_2$) afforded bis(2,2′-biphenylelene)dichloropertellurane **3** in 50% yield together with unknown colorless powder as a byproduct.[4] By the reinvestigation of the unknown colorless powder, we had succeeded in the characterization of the new spirooxytellurane [10-Te-4(C3O)],[5] in which the $SO_3$ unit was inserted between the carbon–tellurium bond in **1**. In this article, we report the isolation and structural determination of new spirooxytellurane **2**.

## RESULTS AND DISCUSSION

Bis(2,2′-bipenylylene)tellurane **1** was treated with an equimolar amount of sulfuryl chloride ($SO_2Cl_2$) in dry THF under −78 °C. After elevating to room temperature, the colorless powder precipitated gradually. As we reported previously,[4] bis(2,2′-biphenylylene)dichloropertellurane **3** was obtained from the organic layer and was recrystallized from THF/$CH_2Cl_2$ solvents. Meanwhile, the unknown product in solution was collected by filtration in air to give the colorless powder as an air- and moisture-stable product. The colorless powder has a poor solubility in nonpolar organic solvents, but dissolved in dimethylsulfoxide (DMSO) and methanol (MeOH). The colorless powder was recrystallized from MeOH to give the spirooxytellurane **2** in 40% yield as shown in Scheme 1. The $^1H$ and $^{13}C$ NMR spectra of **2** in the aromatic region revealed that two kinds of biphenylylene groups exist in this molecule. The signals of each phenyl ring in one biphenylylene group appear separately and those of the other one appear identically. There are two doublet and two triplet peaks as double proton intensity and four doublet and four triplet peaks as single proton intensity in the $^1H$ NMR spectrum. These results indicate that one biphenylylene ligand on the central tellurium atom is symmetrical and the other one is asymmetrical. Moreover, it seems that Berry pseudorotation should take place rapidly in the NMR time scale in solution. The $^{125}Te$ NMR chemical shift of **2** appears at 764.4 ppm, which is little lower than those of previously reported monocarboxyloxytelluranes (2,2′-biphenylylene)(2-biphenylyl)acetyloxytellurane ($\delta$ 720.2) and (2,2′-biphenylylene)(2-biphenylyl)benzolyoxytellurane ($\delta$ 714.5).[6c] **2** was characterized by the parent peak in FABMS spectrum having the identical isotope patterns with that of the calculated one. In addition, **2** was also identified by elemental analysis. A plausible reaction mechanism for the formation of **2** seems to be the following pathway: The lone electron



**Scheme 1**

pair of central tellurium atom of **1** may attack the sulfur atom of $SO_2$, which is generated from $SO_2Cl_2$, and the ligand coupling reaction between carbon and sulfur atoms proceeds, and the oxygen atom in $SO_2$ unit attacks to the tellurium atom. Finally, the preproduced spirooxytellurane having the $SO_2$ unit is probably oxidized in the air to give the final product **2**.

## Crystal Structure

Single crystals of **2** were formed by recrystallization from $CH_3OH$ at room temperature. X-ray crystallographic analysis was employed to determine the unusual structure of **2**. Figure 1 shows an ORTEP plot of the molecular structure of spirooxytellurane **2**. The unit cell of **2** consists of four $[C_{24}H_{16}SO_3]$ molecules containing one $CH_3OH$ molecule.

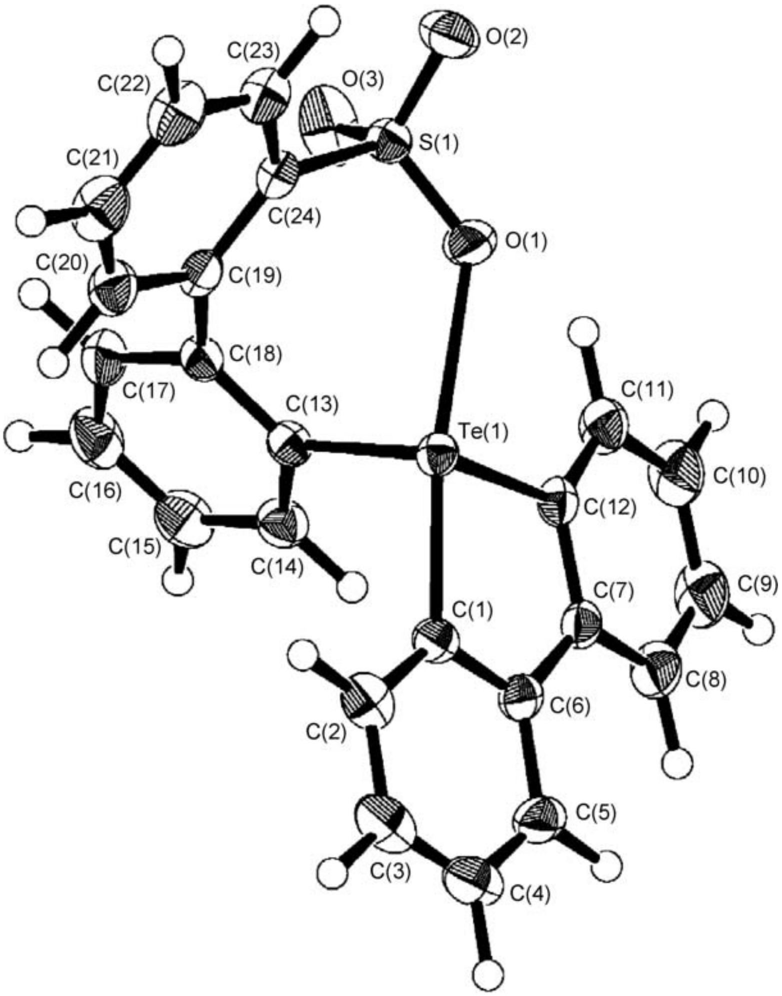


**Figure 1** ORTEP drawing of **2** with the thermal ellipsoids shown at the 50% probability level. For clarity, the containing methanol molecule is omitted.

**Table I** Selected bond lengths, angles, and dihedral angle of **2**

| | |
|---|---|
| Bond length (Å) | |
| Te(1)—O (1) | 2.616 (3) |
| Te(1)—C (1) | 2.106 (3) |
| Te(1)—C(12) | 2.095 (3) |
| Te(1)—C(13) | 2.129 (3) |
| Te(1)—O(2′) | 3.062 (3) |
| Bond angles (°) | |
| O(1)—Te(1)—C (1) | 161.1 (1) |
| C(12)—Te(1)—C(13) | 94.7 (1) |
| O(1)—Te(1)—C(12) | 81.9 (1) |
| O(1)—Te(1)—C(13) | 79.5 (1) |
| C(1)—Te(1)—C(12) | 81.6 (1) |
| C(1)—Te(1)—C(13) | 97.8 (1) |
| Dihedral angle (°) | |
| C(13)—C(18)—C(19)—C(20) | 67.1 (1) |

The $SO_3$ unit, which was inserted between one tellurium—carbon bond, constitutes the seven-membered ring containing a tellurium atom, and one apical position on the central tellurium atom is occupied by an oxygen atom in $SO_3$ unit. The selected bond lengths and angles of **2** are summarized in Table I. The Te(1)—O(1) bond length of **2** is 2.616(3) Å,

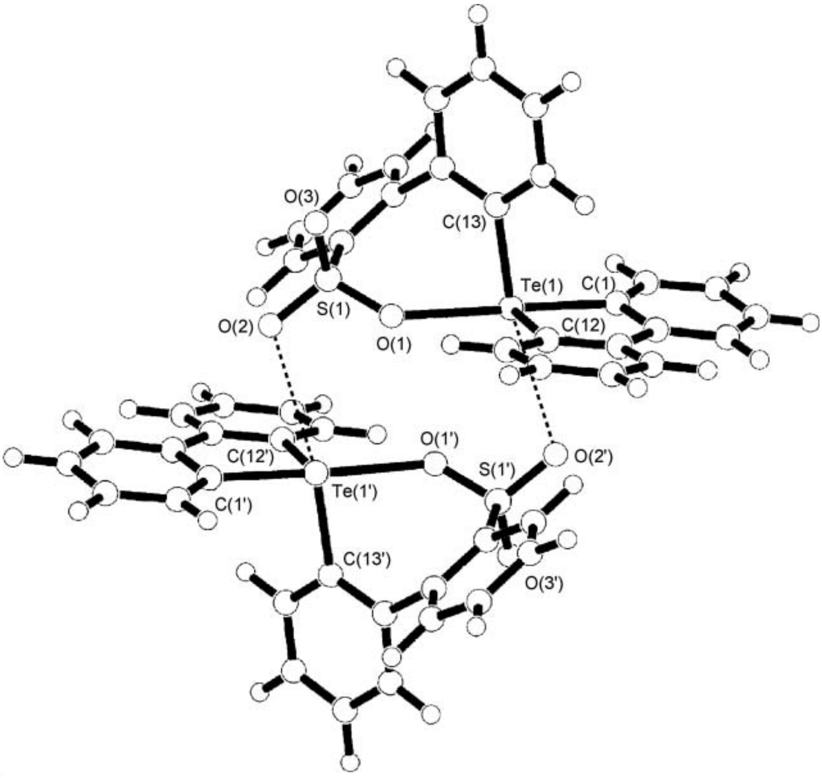


**Figure 2** Intermolecular structure of **2** in the crystal lattice. For clarity, the containing methanol molecule is omitted.

**Table II** X-ray crystallographic data for diffraction studies of **2**

| | |
|---|---|
| Empirical formula | $C_{25}H_{20}O_4STe$ |
| Formula weight | 544.09 |
| Crystal color | Colorless |
| Habit | Prismatic |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ (No.14) |
| Lattice parameter | $a = 11.220(4)$ Å<br>$b = 13.721(3)$ Å<br>$c = 14.314(5)$ Å<br>$\beta = 100.34(3)^\circ$<br>$V = 2167(1)$ Å$^3$ |
| $Z$ value | 4 |
| $D_{\mathrm{calcd}}$ | 1.668 g/cm$^3$ |
| $F(000)$ | 940.00 |
| Temperature | 296 K |
| Radiation | Mo$K\alpha$ ($\lambda = 0.71069$ Å) |
| Crystal dimensions | 0.20 × 0.30 × 0.35 mm |
| $\mu$(Mo$K\alpha$) | 14.99 cm$^{-1}$ |
| Scan type | $\omega$-$2\theta$ |
| Scan rate | 8-5 deg/min |
| Scan width | $(1.57 + 0.30 \tan\theta)^\circ$ |
| $2\theta_{\max}$ | 60.9° |
| Structure solution | Direct methods |
| Total no. of reflections | 7141 |
| No. of unique reflections | 6834 |
| No. of parameters refined | 281 |
| Reflections included | 5545 with $Fo^2 > 4.00\sigma(Fo^2)$ |
| Agreement factors $R$ | 0.030 |
| Agreement factors $R_w$ | 0.034 |

which is much longer than that of the Te—O single covalent bond (2.101 Å),[6] but agrees with the apical Te—O bond length of the 10—Te—4(C3O) species, which has an electron-withdrawing substituent on an oxygen atom.[6] The Te(1)—C(1) bond length as another apical site is 2.106(3) Å, which is a bit shorter than that of the Te—C single covalent bond (2.123 Å).[7]

The apical bond angle O(1)—Te(1)—C(1) and the equatorial bond angle C(12)—Te(1)—C(13) for **2** are 161.1(1)° and 94.7(1)°, respectively. These values indicate that **2** adopts the distorted TBP structure, which is very close to those of **1**,[6a] tetraphenyltellurane,[8] and monocarboxyloxytelluranes,[6c] whose structures have already been determined previously by X-ray crystallographic analysis.

In the crystal lattice, **2** exists as a dimer as a result of the secondary bond formation between the tellurium and an oxygen of $SO_3$ unit of neighboring molecules as shown in Figure 2. The closest intermolecular approach, Te(1)—O(2′), is 3.062(3) Å. This Te(1)—O(2′) distance is between the sum of the 1,3-intramorecular nonbonded radii (2.87 Å) and van der Waals radii (3.60 Å) in the Te—O bond[7] and is similar to that of (2,2′-biphenylylene)(2-biphenylyl)acetyloxytellurane (3.046 Å)[6c] bearing a dimerized environment. Generally, the length of an apical bond in a hypercoordinated compound is longer than that of the equatorial bond. However, the length of the equatorial bond Te(1)—C(13) of **2** is a bit longer than that of an apical bond Te(1)—C(1). This result indicates that the Te(1)—C(13) bond is labilized by the coordination of oxygen O(2′) in the neighboring molecule to the tellurium atom, in other words, by trans effect. The containing $CH_3OH$ molecule is located close to the $SO_3$ unit. The other oxygen of $SO_3$ unit makes a hydrogen bond to the hydrogen of a hydroxyl group in $CH_3OH$. The crystallographic details of **2** are given in Table II.

In conclusion, we succeeded in the isolation and characterization of the novel spirooxytellurane **2** [10–Te–4(C3O)] having a $SO_3$ unit at the apical site, which was prepared by the treatment of tellurane **1** with $SO_2Cl_2$ with pertellurane **3**. The structure of the product **2** was assigned by various NMR experiments, mass spectroscopy, and elemental analysis. A single crystal of **2** was subjected to X-ray crystallographic analysis, which revealed that it crystallizes as a dimer, and that its tellurium center has a distorted trigonal-bypyramidal structure. Further investigation into the chemistry of tellurane having only carbon ligands is in progress.

## EXPERIMENTAL

The $^1H$, $^{13}C$, and $^{125}Te$ NMR were recorded on a JEOL EX-270 NMR, Bruker MSL-400 NMR spectrometer. FABMS spectrum was measured with JEOL JMS-SX102 spectrometer. $^1H$ and $^{13}C$, or $^{125}Te$ NMR data are reported in parts per million (ppm) downfield of TMS or dimethyl telluride. The melting point was measured using Laboratory Devices model MeI-Temp II apparatus. The elemental analysis was performed at the analytical center at the University of Tsukuba.

### Spirooxytellurane 2

To a solution of bis(2,2′-biphenylene)tellurane (**1**) (85 mg, 0.20 mmol) in dry THF (8 ml) at −78°C under an atmosphere of argon, sulfuryl chloride (16 $\mu$l, 0.20 mmol) was added via syringe. The reaction mixture was stirred for 5 h at −78°C. After elevating to room temperature, the colorless powder precipitated in yellow solution. The suspension was exposed to the air and was collected by filtration. The product was recrystallized from methanol to give the spirooxytellurane **2** (33 mg) in 40% yield as a colorless crystal. Mp 322°C (dec.). $^1H$ NMR (400 MHz, DMSO-$d_6$, r.t.) $\delta$ 6.75 (d, $J = 7.6$ Hz, 1H, ArH), 7.16 (t, $J = 7.6$ Hz, 1H, ArH), 7.38 (d, $J = 7.6$ Hz, 1H, ArH), 7.48 (d, $J = 7.6$ Hz, 1H, ArH), 7.49 (t, $J = 7.6$ Hz, 1H, ArH), 7.53 (t, $J = 7.6$ Hz, 1H, ArH), 7.68 (t, J = 7.6 Hz, 1H, ArH), 7.73 (t, J = 7.6 Hz, 1H, ArH), 7.79 (t, J = 7.6 Hz, 1H, ArH), 7.89 (t, $J = 7.6$ Hz, 1H, ArH), 8.05 (d, $J = 7.6$ Hz, 1H, ArH), 8.19 (d, $J = 7.6$ Hz, 1H, ArH), 8.44 (d, $J = 7.6$ Hz, 1H, ArH), 8.48 (d, $J = 7.6$ Hz, 1H, ArH), 8.50 (d, $J = 7.6$ Hz, 1H, ArH). $^{13}C$ NMR (100 MHz, DMSO-$d_6$, r.t.) $\delta$ 125.3, 125.5, 126.7, 128.8, 128.8, 129.9, 130.0, 130.2, 130.7, 138.8, 130.9, 131.8, 132.0, 132.3, 133.6, 133.7, 135.2, 136.2, 138.0, 138.1, 145.1, 146.3, 146.8, 147.1. $^{125}Te$ NMR (126 MHz, DMSO-$d_6$, r.t.) $\delta$ 764.4 (relative to $Me_2Te$). FABMS (*m/z*) 515 $[M+H]^+$ (matrix: 2-nitrophenyl *n*-octyl ether). Anal. Calcd for $C_{24}H_{16}O_3STe \cdot CH_3OH$: C, 55.19; H, 3.70. Found: C, 55.16; H, 3.75.

### Single Crystal X-Ray Analysis of 2

Suitable crystals of **2** were mounted on top of glass fiber, and their respective X-ray data were collected using Rigaku AFC-7R four-circle diffractometer, Mo*Kα* radiation, $\lambda = 0.71069$, $\omega/2\theta$ scan mode, T = 296 K. The structure of **2** was solved by a direct method. All calculations were performed on an Indy workstation using the teXsan crystallographic software package. The crystallographic details are summarized in Table II. Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center (CCDC) as supplementary publication no. CCDC-719736. Copies of the data can be obtained free of charge upon application to CCDC via http://www.ccdc.cam.ac.uk/data_request/cif.

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