the acetate complex,[26] the olefinic bond axis was found to make an angle of 72° with the coordination plane. Perhaps the lengthened palladium-olefin bond length found for the DBMS complex relieves some of the strain in the carbon chain allowing the olefin to adopt a more natural configuration. The palladium-oxygen bond is longer than that found for the allylic complexes[6,7] (π-methallyl)Pd(DBMS), 2.067 (6) Å, and (π-*syn*-1-*tert*-butyl-2-methallyl)Pd(DBMS), 2.047 (7) Å, reflecting the increased trans effect of σ-bonded carbon over allylic-bonded carbon. The palladium-sulfur bond lengths are all very similar for the three complexes.

The olefin bond of the norbornenyl group remains uncoordinated in the solid state, the packing of the molecule being influenced chiefly by van der Waals forces (Figure 5). There are no unusually short nonbonded interatomic distances.

Summary and Conclusions

Allylic palladium complexes containing sulfur-oxygen ligands undergo reactions with dienes similar to those of their dioxygen analogs. This behavior suggests the possibility of many other reactions[27] in which such a substitution is feasible.[28] Intra- and intermolecular exchange in solution prevents determination of the presence of any stereoselective insertion, however, since it cannot be ascertained whether the final product obtained undergoes rearrangement to reach the thermodynamically more stable form. The conformation expected, considering the relative trans-directing abilities of sulfur and oxygen atoms, was realized as evidenced by the low-temperature limiting spectrum of the 1,3-butadiene insertion product as well as the pmr spectrum and solid-state structure of the norbornadiene adduct.

Acknowledgments. Support of this work by the National Science Foundation under Grant GP 27239X2 is gratefully acknowledged.

Registry No. (π-allyl)Pd(TFAS), 41517-11-7; (π-methallyl)Pd(TFAS), 41517-12-8; (π-crotyl)Pd(TFAS), 41517-13-9; (π-allyl)Pd(STTA), 41517-14-0; (π-methallyl)Pd(STTA), 41517-15-1; (π-crotyl)Pd(STTA), 41560-88-7; (1-norbornenyl-2-methylallyl)Pd(DBMS), 41517-16-2; (1-norbornenyl-2-methylallyl)Pd(STTA), 41517-17-3; (π-*syn*-1-(2-methyl-1-butenyl)allyl)Pd(DBMS), 41517-18-4; Pb(TFAS)$_2$, 15744-71-5; Pb(STTA)$_2$, 15282-47-0; (π-methallyl)Pd(DBMS), 32875-75-5; (π-allyl)Pd(TTA), 41517-20-8; (π-methallyl)Pd(TTA), 41517-21-9; di-μ-chloro-di(π-allyl)dipalladium(II), 12012-95-2; di-μ-chloro-di(π-methallyl)dipalladium(II), 12081-18-4; di-μ-chloro-di(π-crotyl)dipalladium(II), 12081-22-0; norbornadiene, 121-46-0; 1,3-butadiene, 106-99-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2659.

(26) M. Zocchi, G. Tieghi, and A. Albinati, *J. Organometal. Chem.*, 33, C47 (1971). Corresponding bond distances: Pd-C1, 2.16 (1) Å; Pd-C2, 2.17 (1) Å; Pd-C10, 2.04 (1) Å.

(27) D. A. White, *J. Chem. Soc. A*, 145 (1971).

(28) In like manner, a sulfur-oxygen ligand may be substituted for the dioxygen ligand in the formation of cationic complexes of the type (1,5-cyclooctadiene)PdCl$_2$ + AgBF$_4$ + HDBMS → [(1,5-cyclooctadiene)Pd(DBMS)]$^+$BF$_4^-$: J. A. Sadownick, unpublished results.

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Crystal and Molecular Structure of 1-Oxa-4-telluracyclohexane 4,4-Diiodide, $C_4H_8OTeI_2$

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The structure of 1-oxa-4-telluracyclohexane 4,4-diiodide, $C_4H_8OTeI_2$, has been determined by use of three-dimensional data collected on an automated X-ray diffractometer with Mo Kα radiation. The space group symmetry is $P2_1/c$ with four molecules in the unit cell for which $a = 8.738$ (2) Å, $b = 7.973$ (2) Å, $c = 14.353$ (3) Å, and $\beta = 110.35$ (1)°. The measured density is 3.20 g cm^{-3} while that calculated from the X-ray data is 3.213 (1) g cm^{-3}. Full-matrix least-squares refinement based on 1661 observed reflections converged to a conventional R index of 3.1%. The molecule closely approximates mirror symmetry through the I, Te, and O atoms with the six-membered ring in the chair form. The bonding about tellurium is octahedral. There are two Te-C bonds at 2.15 (1) and 2.17 (1) Å which make a C-Te-C angle of 94.1 (4)°. Approximately perpendicular to the C-Te-C plane, tellurium forms axial bonds with I(1) at 2.886 (1) Å and I(2) at 2.938 (1) Å, with an I-Te-I angle of 177.08 (4)°. The octahedron about Te is completed through formation of weak intermolecular bonds with an I(1) atom in a second molecule at 3.814 (1) Å and an I(2) atom in a third molecule at 3.692 (1) Å. Other observed distances and angles of interest are as follows: O-C, 1.41 (1) and 1.41 (1) Å; C-C, 1.52 (2) and 1.52 (2) Å; C-H (average), 0.96 (12) Å; C-O-C, 114.2 (8)°; O-C-C, 113.5 (9) and 114.0 (9)°; Te-C-C, 112.8 (6) and 113.5 (7)°.

Introduction

Although the syntheses of 1-oxa-4-telluracyclohexane (1,4-oxatellurane) and several of its derivatives were reported almost 30 years ago,[3] no structural study involving this interesting ring system has been published. Such a study has been the main objective of the present research, but an important second objective has been an investigation of the intermolecular bonding between the heavy atoms which usually occurs in organochalcogen halides.[4-8]

(1) Contribution No. 3123 from the UCLA Department of Chemistry.

(2) (a) University of California, Davis. (b) University of California, Los Angeles.

(3) W. V. Farrar and J. M. Gulland, *J. Chem. Soc.*, 11 (1945).

(4) C. Knobler and J. D. McCullough, *Inorg. Chem.*, 11, 3026 (1972).

(5) J. D. McCullough, Abstracts, Winter Meeting, American Crystallographic Association, Albuquerque, N. M., April 3-7, 1972, Paper K-9.

(6) C. Knobler, J. D. McCullough, and H. Hope, *Inorg. Chem.* 9, 797 (1970).

Table I. Atomic Positional Parameters in $C_4H_8OTeI_2$

Atom	x	y	z
Te	0.17104 (7)[a]	0.34741 (8)	0.13286 (4)
I(1)	0.07251 (10)	0.07176 (10)	0.22960 (6)
I(2)	0.25815 (8)	0.63836 (9)	0.03595 (5)
O	0.4782 (8)	0.1333 (9)	0.1005 (6)
C(1)	0.4245 (12)	0.3091 (14)	0.2260 (7)
C(2)	0.5335 (13)	0.2702 (15)	0.1664 (9)
C(3)	0.3535 (16)	0.1747 (14)	0.0100 (10)
C(4)	0.1847 (13)	0.1837 (13)	0.0171 (8)
H(1A)[b]	0.428 (12)	0.228 (13)	0.275 (7)
H(1B)	0.444 (11)	0.430 (13)	0.264 (7)
H(2A)	0.650 (12)	0.232 (12)	0.234 (7)
H(2B)	0.534 (13)	0.353 (13)	0.138 (8)
H(3A)	0.332 (12)	0.075 (13)	−0.033 (7)
H(3B)	0.374 (15)	0.255 (15)	−0.011 (9)
H(4A)	0.103 (12)	0.203 (13)	−0.053 (8)
H(4B)	0.144 (12)	0.080 (13)	0.020 (7)

[a] The numbers given in parentheses here and in succeeding tables are the estimated standard deviations in the least significant digits.
[b] Hydrogen atoms are numbered to correspond to the carbon atoms to which they are bonded.

Table II. Atomic Thermal Parameters in $C_4H_8OTeI_2$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Te	92 (1)	104 (1)	35 (1)	13 (2)	51 (1)	−1 (1)
I(1)	213 (2)	164 (2)	66 (1)	−53 (3)	124 (2)	44 (1)
I(2)	106 (1)	131 (1)	51 (1)	−18 (2)	37 (1)	31 (1)
O	123 (12)	148 (14)	70 (5)	75 (22)	62 (13)	−17 (15)
C(1)	118 (17)	134 (20)	25 (5)	−5 (30)	−2 (15)	3 (16)
C(2)	83 (16)	139 (21)	69 (8)	18 (32)	46 (19)	13 (22)
C(3)	143 (20)	135 (23)	55 (8)	11 (37)	94 (21)	−19 (22)
C(4)	109 (17)	118 (19)	39 (6)	−40 (29)	47 (16)	−44 (18)

[a] All parameters have been multiplied by 10^4. The anisotropic temperature factor expression is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. The hydrogen atoms were assigned fixed isotropic thermal parameters of 5.0 Å^2.

Experimental Section

The 1,4-oxatellurane was synthesized by a method similar to that of Farrar and Gulland[3] but the yield and purity of the product were both improved by excluding oxygen as in the 1,4-thiatellurane synthesis[9] and isolating the product by the steam distillation procedure used for 1,4-oxaselenane.[10] The liquid is colorless when pure, not lemon yellow[11] as described by Farrar and Gulland.

Crystals of 1,4-oxatellurane diiodide were prepared by mixing solutions of the components (1,4-oxatellurane and iodine) in ethylene chloride in closely 1:1 stoichiometry. (Excess iodine must be avoided as dark higher iodides are then formed.) The crystals, when thus prepared, are bright red prisms, in strong contrast to those of 1,4-thiatellurane diiodide which are dark purple needles with a metallic luster.[6] After recrystallization from ethylene chloride by slow evaporation of the solvent, specimens were selected for the X-ray study. A preliminary examination by means of Weissenberg and precession photographs showed monoclinic symmetry and the systematic extinction of $0k0$ with k odd and $h0l$ with l odd indicated the space group $P2_1/c$. The specimen selected for intensity measurements was a prism 0.10 × 0.10 × 0.25 mm along a, b, and c respectively and was mounted with c close to the ϕ axis of a Picker full-circle automated diffractometer. Crystal setting parameters and cell dimensions were obtained by a least-squares fit to 18 sets of measured diffractometer angles. The resulting cell dimensions, based on Mo Kα radiation (λ 0.71069 Å), are $a = 8.738$ (2) Å, $b = 7.973$ (2) Å, $c = 14.353$ (3) Å, and $\beta = 110.35$ (1)°. The density observed by flotation in a mixture of methylene iodide and bromoform is 3.20 g cm^{-3}, which compares favorably with the value 3.213 g cm^{-3} calculated from the above cell parameters with $Z = 4$. Thus, there is one formula unit of $C_4H_8OTeI_2$ in the asymmetric unit and no molecular symmetry is crystallographically required.

The intensities of all 1929 unique reflections accessible with $2\theta \leqslant 53°$ were measured with the diffractometer in automatic mode. The radiation was graphite-monochromatized Mo Kα in conjunction with a pulse height analyzer. The takeoff angle was 3.5°. The θ–2θ scan technique was used with a 2θ scan rate of 1°/min and a scan range from 0.8° below the Kα_1 peak to 0.8° above the Kα_2 peak. Background counts were taken for 20 sec at each end of the scan range and the automatic attenuator mechanism was set to keep the count rate below 10,000 counts/sec. The intensities of two reference reflections were measured after every 120 reflections and no systematic drift was noted. Several of the weaker reflections were remeasured at the end and there were no significant changes from initial values. The calculated value for μ for Mo Kα radiation is 100 cm^{-1}. Empirical absorption corrections were applied to all data on the basis of the experimentally observed variations in the intensities of the $00l$ reflections as a function of ϕ. The corrections covered a range of ±6%, relative.

On the basis of the stability noted during this and previous runs with the diffractometer, each recorded number of counts, N, was assigned an estimated standard deviation, $\sigma(N) = [N + (0.005N)^2]^{1/2}$. The net intensities were calculated by use of the equation

$$I = N - (t_s/2t_b)(B_1 + B_2)$$

in which B_1 and B_2 are the individual background counts, t_s is the scan time (seconds) and t_b is the time (20 sec) each background is counted. A total of 1661 unique reflections for which the net intensity was greater than 3σ were recorded as "observed." The remaining 268 measured reflections were considered "unobserved" and were omitted from the least-squares refinement.

Determination and Refinement of the Structure

The structure was determined by the application of heavy-atom methods to Patterson and Fourier summations.[12] Refinement was carried out by use of full-matrix least-squares procedures with anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) applied to the form factors for tellurium and iodine. After several cycles of refinement with anisotropic temperature factors on all nonhydrogen atoms, R converged to 0.040. A comparison of $|F_o|$ and $|F_c|$ values at this point suggested that many of the stronger, low-order reflections were being affected by secondary extinction; the intensities of all observed reflections were therefore processed by SECEXT.[13] In order to locate the hydrogen atoms, a difference Fourier map was calculated and the peaks were compared with a set of positions calculated by use of HPOSN. All eight hydrogen atoms showed on the Fourier close to their expected positions with maxima in the range from 0.4 to 0.6 e/Å^3. Three more cycles of least-squares refinement were then computed in which the positional (but not the thermal) parameters of the hydrogen atoms were allowed to vary, along with the positional and anisotropic thermal parameters of the eight heavier atoms. In these cycles, the hydrogen atoms were assigned fixed isotropic thermal parameters of 5.0 Å^2. The R index decreased to its final value of 0.031. A set of structure factors[14] for all measured reflections was calculated on the basis of the final positional and thermal parameters given in Tables I and II. The atomic scattering factors used for iodine were the I^0

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(7) H. Hope and J. D. McCullough, *Acta Crystallogr.*, **17**, 712 (1964).

(8) G. Y. Chao and J. D. McCullough, *Acta Crystallogr.*, **15**, 887 (1962).

(9) J. D. McCullough, *Inorg. Chem.* 4, 862 (1965).

(10) J. D. McCullough and A. Lefohn, *Inorg. Chem.*, **5**, 150 (1966).

(11) Organotellurides have been observed in these laboratories to form stable, yellow adducts with sulfur dioxide. The color of Farrar and Gulland's product was doubtless due to contamination by sulfur dioxide from the potassium metabisulfite they used in reducing the oxatellurane dichloride.

(12) Fourier summations were computed by use of UCLAFOUR written by Gantzel and Hope and the least-squares refinement was carried out by using CADLS, the centric, anomalous dispersion modification (by Hope, Black, and Frank) of the full-matrix program UCLALS4 by Gantzel, Sparks, Long, and Trueblood. This program minimizes $\Sigma w(kF_o - |F_c|)^2$, where k is a scale factor. The weights, w, were taken as $1/\sigma^2(F_o)$. The esd values for the atomic parameters were obtained from the final least-squares inverse matrix and those for bond distances and angles were derived by use of a modification of ORFFE by Busing, Martin, and Levy. Thermal ellipsoid plots were prepared by use of Johnson's ORTEP and tentative hydrogen positions were computed by use of HPOSN by Hope. The C–H distances were taken initially as 1.0 Å and the H–C–H angles as 109.5°. Corrections for the effects of secondary extinction were calculated by use of Christensen's SECEXT program and the R index is defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.

(13) In this program, secondary extinction corrections are computed by use of the expression $F_{cor} = F_o(1 + C\beta J_o)^{1/2}$, the symbols in which are defined by W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963). In the present case the coefficient C had the value 1.47×10^{-6} and the maximum correction in an F_o value was 34%.

(14) See paragraph at end of paper regarding supplementary material.

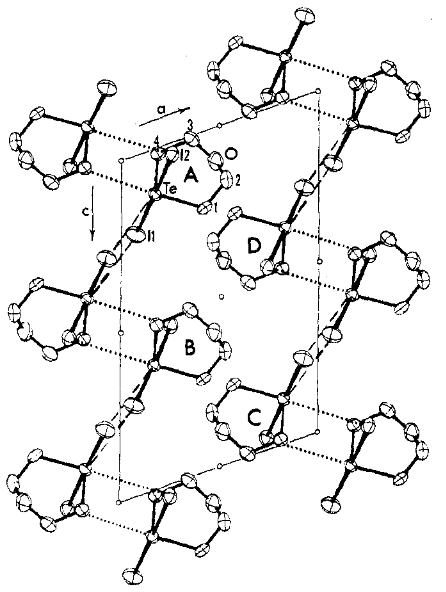

Figure 1. ORTEP plot of the structure of $C_4H_8OTeI_2$ viewed down the *b* axis. The thermal ellipsoids in this and the following figures are drawn at the 50% probability level. Secondary Te–I bonds between molecules related by centers of symmetry are shown by means of dotted lines while those along the twofold screw axes are indicated by dashed lines. The symmetry positions A, B, C, and D are defined in Table III. Carbon atoms are indicated by the numbers 1–4.

values of Doyle and Turner[15] and their values for Sb^0 and I^0 were averaged to give a set of values for tellurium. The neutral atom values given in Table 3.3.1A of ref 16 were used for oxygen, the factors for carbon were the diamond values of McWeeny,[17] and the hydrogen factors were from Stewart, Davidson, and Simpson.[18] The real and imaginary anomalous dispersion corrections given for Mo Kα radiation in Table 3.3.2C of ref 16 were applied to the scattering factors for Te and I. An analysis of the values of $|F_c|$ and $|F_o|$ for the "unobserved" reflections showed all 268 values of $|F_c|$ to be less than 11.2, 186 reflections (69%) showed $|F_c| \leqslant |F_o|$, and there was no case with $|F_c| > 2|F_o|$. In the final least-squares cycle, the largest shift of a parameter for a nonhydrogen atom was 0.3σ for positional parameters and 0.5σ for thermal parameters. The average shift in the 24 positional parameters of the hydrogen atoms was 0.45σ with two showing shifts slightly larger than σ. The final difference summation showed residuals in the range from −0.6 to +0.6 e/Å^3, most of which were in the immediate vicinity of the Te and I atoms. The esd of the electron density was 0.3 e/Å^3.

Description and Discussion of the Structure

Views of the crystal structure of $C_4H_8OTeI_2$ down the *b* and *a* axes are shown in Figures 1 and 2, respectively, and the molecule, the 1,4-oxatellurane ring, and the coordination about tellurium are shown in Figures 3–5. Bond distances, bond angles, torsion angles, and some intramolecular atomic separations are given in Tables III–V. The root-mean-square amplitudes of vibration of the nonhydrogen atoms are given in Table VI.

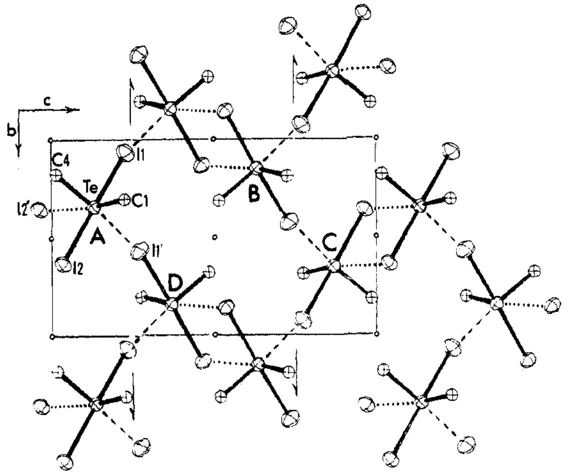

Figure 2. View down the *a* axis of $C_4H_8OTeI_2$ showing one of the two-dimensional networks formed by the Te–I secondary bonds. For purposes of clarity, only those atoms directly bonded to tellurium are included. Atoms C(1) and C(4) are shown with artifically small isotropic temperature parameters. Their true anisotropic thermal ellipsoids are shown in other figures.

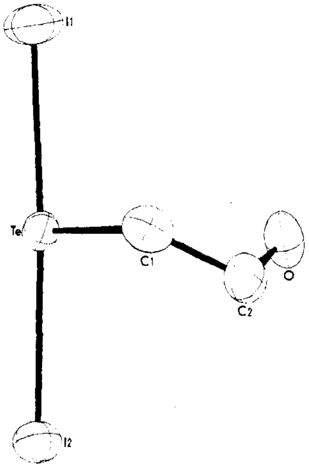

Figure 3. View of the $C_4H_8OTeI_2$ molecule normal to the approximate mirror plane of symmetry. The eclipsed carbon atoms C(3) and C(4) are omitted for clarity.

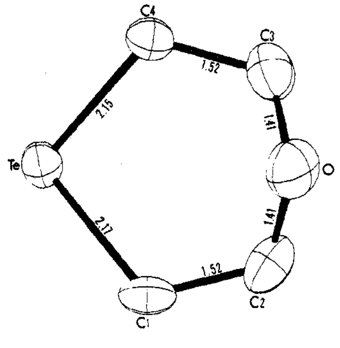

Figure 4. The 1,4-oxatellurane ring in $C_4H_8OTeI_2$ as viewed normal to the plane of the carbon atoms.

Although not crystallographically required, the $C_4H_8OTeI_2$ molecule approximates closely to mirror symmetry through the I, Te, and O atoms. The small deviations from this symmetry shown by the distances and angles in Tables IV and V are probably below the significance level. The bonding about tellurium in the free $C_4H_8OTeI_2$ molecule might be considered to be trigonal bipyramidal with two carbon atoms and an unshared pair of electrons in the equatorial positions. However, the configuration about tellurium in the crystalline solid is probably best described as octahedral. There are two normal covalent bonds to carbon atoms with observed distances of 2.15 and 2.17 Å. The angle between these bonds is 94.1°. Two axial bonds[19] (approximately perpendicular

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[15] P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 392 (1968).

[16] "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

[17] R. McWeeny, *Acta Crystallogr.*, **7**, 180 (1954).

[18] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[19] The term "axial" refers here to the positions in the approximate trigonal bipyramid about tellurium.

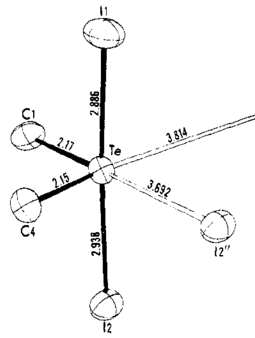

Figure 5. View of the coordination about tellurium. A complete listing of the angles involved is given in Table III.

Table III. Distances and Angles about Tellurium and Iodine Atoms in $C_4H_8OTeI_2$[a]

Distances about Tellurium Atom, Å			
Te–C(1)	2.17 (1)	Te–C(4)	2.15 (1)
Te–I(1)	2.886 (1)	Te–I(2)	2.938 (1)
Te· · ·I(1)′	3.814 (1)	Te· · ·I(2)″	3.692 (1)
Angles about Tellurium Atom, Deg			
C(1)–Te–C(4)	94.1 (4)	I(1)–Te–I(2)	177.08 (4)
C(1)–Te–I(1)	90.4 (3)	C(4)–Te–I(1)	90.9 (3)
C(1)–Te–I(2)	91.5 (3)	C(4)–Te–I(2)	91.2 (3)
C(1)–Te· · ·I(1)′	112.3 (3)	C(4)–Te· · ·I(1)′	151.2 (3)
C(1)–Te· · ·I(2)″	173.3 (3)	C(4)–Te· · ·I(2)″	80.1 (3)
I(1)–Te· · ·I(1)′	78.16 (3)	I(2)–Te· · ·I(1)′	99.08 (3)
I(1)–Te· · ·I(2)″	86.25 (3)	I(2)–Te· · ·I(2)″	92.08 (2)
I(1)′· · ·Te· · ·I(2)″	72.72 (2)		
Distances about Iodine Atoms, Å			
I(1)–Te	2.886 (1)	I(2)–Te	2.938 (1)
I(1)· · ·Te‴	3.814 (1)	I(2)· · ·Te″	3.692 (1)
Angles about Iodine Atoms, Deg			
Te–I(1)· · ·Te‴	156.86 (3)	Te–I(2)· · ·Te″	87.92 (2)

[a] Unprimed atoms are in the $C_4H_8OTeI_2$ molecule in symmetry position A of the origin cell, *i.e.* (A, 000). Atom I(1)′ is in molecule (D, $\bar{1}00$), *i.e.*, the molecule in symmetry position D of the cell located one lattice translation unit in the negative direction along the *a* axis. Atoms with a double prime are in molecule (C, $\bar{1}0\bar{1}$) and Te‴ is in molecule (D, $\bar{1}\bar{1}0$). The symmetry positions have the following coordinates: $A = (x, y, z)$; $B = (x, {}^1/_2 - y, {}^1/_2 + z)$; $C = (1 - x, 1 - y, 1 - z)$; $D = (1 - x, {}^1/_2 + y, {}^1/_2 - z)$. Secondary (intermolecular) bonds are designated thus, Te· · ·I(1)′.

Table IV. Distances and Angles in the 1,4-Oxatellurane Moiety of $C_4H_8OTeI_2$

Distances, Å			
Te–C(1)	2.17 (1)	Te–C(4)	2.15 (1)
O–C(2)	1.41 (1)	O–C(3)	1.41 (1)
C(1)–C(2)	1.52 (2)	C(3)–C(4)	1.52 (2)
C–H (range)	0.76 (13)–1.18 (10)	C–H (av)	0.96 (12)
Bond Angles, Deg			
C(1)–Te–C(4)	94.1 (4)	C(2)–O–C(3)	114.2 (8)
Te–C(1)–C(2)	112.8 (6)	O–C(2)–C(1)	113.5 (9)
Te–C(4)–C(3)	113.5 (7)	O–C(3)–C(4)	114.0 (9)
Torsion Angles, Deg			
Te–C(1)–C(2)–O	−54 (1)		
O–C(3)–C(4)–Te	54 (1)		
C(2)–O–C(3)–C(4)	−81 (1)		
C(1)–C(2)–O–C(3)	81 (1)		
C(3)–C(4)–Te–C(1)	−29 (1)		
C(4)–Te–C(1)–C(2)	29 (1)		
Dihedral Angles between Planes, Deg			
[C(1), C(2), C(3), C(4)]–[C(1), Te, C(4)]	27.5 (8)		
[C(1), C(2), C(3), C(4)] – [C(2), O, C(3)]	70 (1)		

Table V. Some Nonbonded Intramolecular Distances (Å) in $C_4H_8OTeI_2$[a,b]

I(1)–C(4)	3.62 (1)	I(1)–H(1A)	3.2 (1)
I(1)–C(1)	3.63 (1)	I(1)–H(4B)	3.3 (1)
I(2)–C(4)	3.67 (1)	I(2)–H(2B)	3.3 (1)
I(2)–C(1)	3.70 (1)	I(2)–H(3B)	3.4 (1)
I(2)–C(3)	3.84 (1)	Te–H(1B)	2.6 (1)
I(2)–C(2)	3.84 (1)	Te–H(1A)	2.6 (1)
Te–C(3)	3.08 (1)	Te–H(4B)	2.6 (1)
Te–C(2)	3.09 (1)	Te–H(4A)	2.8 (1)
Te–O	3.35 (1)	Te–H(2B)	3.2 (1)
O–C(1)	2.45 (1)	Te–H(3B)	3.2 (1)
O–C(4)	2.46 (1)		

[a] The following sums of van der Waals radii, in Å (ref 20 p 260), are given for comparison (the CH_3 radius is taken for carbon): Te–C and I–C, 4.2; Te–O, 3.60; O–C, 3.4; Te–H and I–H, 3.4. [b] Other than the Te· · ·I secondary bonds listed in Table III, there are no intermolecular contacts significantly below the sums of the corresponding van der Waals radii.

Table VI. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max
Te	0.162	0.183	0.187
I(1)	0.178	0.261	0.277
I(2)	0.185	0.191	0.239
O	0.174	0.235	0.263
C(1)	0.142	0.208	0.229
C(2)	0.166	0.212	0.257
C(3)	0.180	0.215	0.239
C(4)	0.158	0.190	0.223

to the C–Te–C plane) are formed with iodine atoms at 2.886 and 2.938 Å making an angle of 177.08° with each other. The octahedron is completed through intermolecular bonding of Te with an I(1) atom in a neighboring molecule at 3.814 Å and an I(2) atom in a third molecule at 3.692 Å. For comparison, the sum of the normal single-bond radii for Te and I is 2.70 Å and the sum of the van der Waals radii is 4.35 Å.[20] The bond angles which these "secondary" intermolecular bonded atoms make with opposing carbon atoms are C(1)–Te· · ·I(2)″ = 173.3° and C(4)–Te· · ·I(1)′ = 151.2°. Except for three angles involving I(1)′, the remaining bond angles about tellurium are within 10° of the ideal 90° value. A complete listing of the bond distances and bond angles about the tellurium and iodine atoms is given in Table III.

The intermolecular bonding system is indicated by means of dotted and dashed lines in Figures 1 and 2. The stronger secondary bonds are between Te and I(2) atoms and join molecules into pairs across centers of symmetry. These bonds are 3.692 Å long and are represented by dotted lines in the figures. The dashed lines in the figures indicate a second system of secondary bonds which connect molecules along 2_1 screw axes with a Te· · ·I(1)′ separation of 3.814 Å. As a result, the molecules are loosely bonded into layers which extend infinitely along the *b* and *c* crystallographic axes but are only one unit cell thick in the direction of the *a* axis. It is interesting to note that the iodine atom I(1), which forms the stronger axial bond to tellurium, forms the weaker secondary bond. This behavior is reasonable and has been observed in other $R_2(Se,Te)X_2$ compounds studied in this laboratory. It is also interesting that I(2), with the stronger secondary bonds, forms a bond angle Te–I(2)· · ·Te″ of 87.92°, close to one of the angles (90 and 180°) which iodine ideally forms in these circumstances. In contrast, the angle at I(1) is 156.86°, considerably further from an ideal value.

As expected from observations on other $R_2(Se,Te)X_2$ compounds which have been studied, the axial chalcogen–halogen bonds are longer (0.19 and 0.24 Å in the present case) than the sum of the normal, single-bond radii and correspond approximately to a bond order of $^1/_2$.

The bond distances, bond angles, and torsion angles in the

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(20) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 224, 260.

1,4-oxatellurane moiety in $C_4H_8OTeI_2$ are given in Table IV. Although the six-membered ring is in the chair form, the heteroatoms produce marked changes from cyclohexane geometry, as can be noted in Figures 3 and 4. A least-squares plane fitted to the carbon atoms is within 0.004 Å of each of the four atoms, a distance much less than the esd of the carbon positions, 0.011 Å. This least-squares plane makes dihedral angles of 27.5° with the C(1)-Te-C(4) plane and 70° with the C(2)-O-C(3) plane. The Te and O atoms are displaced 0.682 and −0.725 Å, respectively, from the carbon atom plane.

Because of the effects of secondary bonding on the lengths of the axial Te-I bonds, it is not very meaningful to compare the present observed values of 2.886 (1) and 2.938 (1) Å with those observed in previous studies of R_2TeI_2 compounds. However, the present values do fall in the range of values 2.851 (2)-2.985 (2) Å observed in the earlier studies.[5,6,8] While β-dimethyltellurium diiodide has the formal composition Me_2TeI_2, its structure[21] is best described by the ionic formulation $[Me_3Te]^+[MeTeI_4]^-$. In this compound the Te-I bond distances range from 2.840 to 2.984 Å, close to the range of values observed in the nonionic R_2TeI_2 compounds.

It is interesting that the crystal structure of $C_4H_8OTeI_2$ differs so greatly from that of $C_4H_8STeI_2$[6] considering the fact that neither the oxygen atom nor the sulfur atom is involved in any intermolecular bonding or contacts less than the sums of the corresponding van der Waals radii. Apparently the effects of these atoms on the structures are transmitted through tellurium. A similar effect has been noted in the dissociation of $C_4H_8OSeI_2$ and $C_4H_8SSeI_2$ into the selenane and molecular iodine in dilute carbon tetrachloride solution.[22] The former compound has a dissociation constant 44% greater than that of the latter compound at 25°.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2665.

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Crystal and Molecular Structure of Phenoxatellurin 10,10-Diiodide, $C_{12}H_8OTeI_2$[1]

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The structure of phenoxatellurin 10,10-diiodide, $C_{12}H_8OTeI_2$, has been determined by use of three-dimensional X-ray data collected on an automated diffractometer with monochromatized Mo Kα radiation. The space group is $P2_1/n$ with four molecules in the unit cell for which $a = 7.991$ (1) Å, $b = 10.598$ (2) Å, $c = 17.138$ (3) Å, and $\beta = 103.69$ (1)°. The measured and calculated densities are 2.58 (2) and 2.589 (1) g cm^{-3}, respectively. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures to a conventional R index of 4.3%. The phenoxatellurin moiety consists of planar halves with a fold angle of 163.9 (4)° along the line of the shared Te and O atoms. Tellurium forms bonds with carbon atoms at 2.09 (2) and 2.11 (2) Å with a bond angle of 91.5 (6)°. Approximately perpendicular to the C-Te-C plane, Te forms axial bonds with I atoms at 2.945 (2) and 2.941 (2) Å. The I-Te-I angle is 176.44 (6)°. Tellurium also forms weak bonds with iodine atoms in each of two neighboring molecules with Te· · ·I distances of 3.739 and 3.788 Å. The C-Te· · ·I bond angles are 170.9 (6) and 171.0 (5)° so that the configuration about Te is octahedral. The intermolecular Te· · ·I bonds link molecules into infinite chains along the a axis. The observed C-C bond distances range from 1.34 (3) to 1.46 (3) Å with an average of 1.39 Å. The C-O distances are 1.34 (2) and 1.37 (2) Å with a C-O-C bond angle of 125 (1)°.

Introduction

Structural studies of di-p-chlorophenyltellurium diiodide,[2] 1-thia-4-telluracyclohexane 4,4-diiodide,[3] and 1-oxa-4-telluracyclohexane 4,4-diiodide[4] have shown that these compounds have extensive intermolecular bonding systems involving the heavy atoms. Crystals of the first two compounds are dark violet and the second shows a definite metallic luster. The intermolecular bonding in these crystals consists mainly of nearly linear chains of the type · · ·I-Te-I· · ·I-Te-I· · · with secondary I· · ·I bonds. In contrast, the third (or oxa) compound is bright red and the intermolecular bonds have been found to consist of Te· · ·I interactions only. Interestingly, solutions of all molecular[5] R_2TeI_2 compounds in organic solvents are yellow to orange. This suggests that the color of

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(5) Some modifications of alkyl R_2TeI_2 compounds are ionic. For example, crystals of β-$(CH_3)_2TeI_2$ have been shown to consist of $(CH_3)_3Te^+$ and $CH_3TeI_4^-$ ions: F. Einstein, J. Trotter, and C. Williston, *J. Chem. Soc. A*, 2018 (1967).