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**Supplementary Material Available:** A listing of structure factor amplitudes (Table II) (8 pages). Ordering information is given on any current masthead page.

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## Crystal and Molecular Structure of Phenoxatellurin 10,10-Dichloride

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The crystal structure of phenoxatellurin 10,10-dichloride,  $\text{C}_{12}\text{H}_8\text{OTeCl}_2$ , has been determined by X-ray single-crystal diffraction. The crystals are triclinic of space group  $P\bar{1}$  ( $Z = 4$ ) with  $a = 8.555$  (9) Å,  $b = 12.628$  (10) Å,  $c = 13.778$  (9) Å,  $\alpha = 105.25$  (5)°,  $\beta = 95.65$  (7)°, and  $\gamma = 103.75$  (8)°. In the solid state the molecules arrange themselves into discrete tetrameric clusters via  $\text{Te}\cdots\text{Cl}$  secondary bonding. The Te coordination is then a slightly distorted octahedron, with primary bonds to two phenyl carbons and two chlorines, and secondary bonds to two chlorines on adjacent molecules. There are three different types of chlorines present, having 0, 1, or 2 secondary bonds to chlorine, respectively, and the primary Te-Cl bond length is found to be a function of this. The  $\text{M}_4\text{X}_6$  core is arranged in a "step" structure as opposed to a "cubane" structure, possibly due to the bulk of the attached ring system. The fold angle of the two phenyl rings at the  $\text{Te}\cdots\text{O}$  vector is about 151°, and it seems plausible that the degree of folding in this and related compounds is a function of the electronegativity of the substituent groups.

### Introduction

As part of a study concerning group 6A shielding coefficients and, specifically, C-Te coupling constants, phenoxatellurin 10,10-dichloride was synthesized as an intermediate leading to the reduced species phenoxatellurin,  $\text{C}_{12}\text{H}_8\text{OTe}$ . It was noted, however, that the 10,10-dichloride yielded both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra that were extraordinarily broadened and uninterpretable, almost as if the compound was paramagnetic or was involved in some equilibrium process on the order of the NMR time scale. The X-ray crystal structure was thus undertaken to help elucidate the nature of the intermolecular interactions involved. Several examples of polymer- and cluster-forming tellurium compounds are known,<sup>2-8</sup> and so it was assumed that the 10,10-dichloride would also arrange itself into some lowest energy configuration, probably with bridging chlorines. This was found to be the case, although somewhat more complicated than anticipated.

### Experimental Section

**Synthesis and Spectra.** The synthesis of phenoxatellurin 10,10-dichloride was achieved by condensing anhydrous tellurium tetrachloride in neat refluxing diphenyl ether according to the general

Table I. Summary of Data Collection and Processing Parameters

space group	$P\bar{1}$ , triclinic
cell constants	$a = 8.555$ (9) Å, $\alpha = 105.25$ (5)°, $b = 12.628$ (10) Å, $\beta = 95.65$ (7)°, $c = 13.778$ (9) Å, $\gamma = 103.75$ (8)°, $V = 1374.2$ Å <sup>3</sup> , $Z = 4$
molecular formula	$\text{C}_{12}\text{H}_8\text{OTeCl}_2$
mol wt	366.70
density (calcd)	$\rho = 1.77$ g cm <sup>-3</sup>
abs coeff	$\mu = 23.47$ cm <sup>-1</sup>
data collectn range	$5^\circ \leq 2\theta \leq 50^\circ$
scan width	$\Delta\theta = (1.10 + 0.35 \tan \theta)^\circ$
max scan time	300 s
scan speed range	0.3-3.4° min <sup>-1</sup>
total data collected	4744
data with $I > 3\sigma(I)$	3678
total variables	289
$R = \sum   F_o  -  F_c   / \sum  F_o $	0.047
$R_w = [\sum w( F_o  -  F_c )^2]^{1/2} / \sum w F_o ^2$	0.050
weights	$w = \sigma( F )^{-2}$

procedure of Drew.<sup>9</sup> The crude, isolated phenoxatellurin 10,10-dichloride was recrystallized from toluene. Spectral acquisition was attempted with a solution of phenoxatellurin 10,10-dichloride in deuteriochloroform. No usable or interpretable resonances were observed in either the 100.06-MHz  $^1\text{H}$  NMR or 25.158-MHz  $^{13}\text{C}$  NMR spectra. Attempts were also made to observe the 30.106-MHz  $^{125}\text{Te}$  NMR spectrum which likewise proved to be fruitless. Efforts are presently underway, however, to observe the  $^{13}\text{C}$  NMR spectrum in the solid state with magic angle spinning, and these results will be reported elsewhere.

**X-ray Crystallography.** The single crystal used for data collection was a clear, yellow plate of approximate dimensions 0.60 × 0.50 ×

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Table II. Atomic Coordinates and Thermal Parameters ( $\times 1000$ ; Te,  $\times 10\ 000$ )

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Te1	0.37447 (7)	0.10775 (4)	0.26976 (4)	347 (3)	331 (3)	454 (3)	69 (2)	43 (3)	136 (3)
Cl1A	0.2511 (3)	-0.0052 (2)	0.3879 (2)	57 (1)	37 (1)	51 (1)	13 (1)	11 (1)	18 (1)
Cl2A	0.4820 (3)	0.2202 (2)	0.1562 (2)	73 (2)	70 (2)	82 (2)	12 (1)	31 (2)	45 (2)
O1	-0.0281 (8)	0.0365 (5)	0.2197 (6)	45 (4)	45 (4)	89 (5)	-3 (3)	9 (4)	7 (4)
C1A	0.2063 (10)	0.2014 (7)	0.3035 (6)	38 (5)	39 (5)	42 (5)	12 (4)	10 (4)	23 (4)
C2A	0.2586 (10)	0.3171 (7)	0.3569 (7)	36 (5)	35 (5)	64 (6)	11 (4)	3 (4)	17 (4)
C3A	0.1517 (14)	0.3786 (8)	0.3863 (8)	77 (8)	43 (5)	66 (7)	20 (5)	21 (6)	28 (5)
C4A	-0.0236 (13)	0.3199 (10)	0.3549 (9)	67 (7)	74 (7)	84 (8)	44 (6)	31 (6)	42 (6)
C5A	-0.0714 (11)	0.2082 (9)	0.2999 (9)	36 (5)	59 (7)	84 (8)	6 (5)	11 (5)	25 (6)
C6A	0.0367 (11)	0.1469 (7)	0.2733 (7)	40 (5)	42 (5)	53 (6)	6 (4)	7 (4)	16 (4)
C7A	0.0409 (12)	-0.0256 (7)	0.1448 (8)	47 (6)	39 (5)	62 (6)	2 (4)	4 (5)	23 (5)
C8A	-0.0720 (14)	-0.1099 (9)	0.0659 (9)	70 (7)	52 (6)	67 (7)	-10 (5)	-9 (6)	11 (6)
C9A	-0.0163 (17)	-0.1745 (9)	-0.0114 (9)	92 (10)	44 (6)	70 (8)	5 (6)	-24 (7)	3 (6)
C10A	0.1499 (17)	-0.1587 (9)	-0.0132 (8)	108 (10)	47 (6)	52 (7)	25 (6)	-5 (7)	7 (5)
C11A	0.2624 (12)	-0.0787 (7)	0.0676 (7)	69 (7)	36 (5)	47 (6)	11 (5)	5 (5)	12 (4)
C12A	0.2056 (11)	-0.0138 (7)	0.1462 (7)	51 (6)	32 (5)	49 (6)	2 (4)	2 (5)	19 (4)

atom	<i>x</i>	<i>y</i>	<i>z</i>	atom	<i>x</i>	<i>y</i>	<i>z</i>
H2A <sup>a</sup>	0.378	0.356	0.374	H8A	-0.192	-0.122	0.066
H3A	0.192	0.461	0.428	H9A	-0.097	-0.235	-0.068
H4A	-0.107	0.362	0.374	H10A	0.187	-0.205	-0.072
H5A	-0.191	0.169	0.278	H11A	0.383	-0.069	0.069

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Te2	0.50252 (6)	0.18048 (4)	0.61384 (4)	337 (3)	299 (3)	445 (3)	77 (2)	28 (3)	85 (2)
Cl1B	0.4001 (3)	0.0925 (2)	0.7463 (2)	57 (2)	53 (1)	91 (2)	17 (1)	24 (1)	39 (1)
Cl2B	0.6193 (3)	0.2821 (2)	0.4877 (2)	40 (1)	67 (2)	47 (1)	9 (1)	5 (1)	17 (1)
O2	0.5300 (8)	0.4552 (5)	0.6949 (5)	51 (4)	37 (3)	67 (4)	5 (3)	-11 (3)	19 (3)
C1B	0.3271 (10)	0.2717 (7)	0.6233 (6)	38 (5)	39 (5)	40 (5)	15 (4)	5 (4)	14 (4)
C2B	0.1617 (11)	0.2113 (8)	0.5917 (7)	37 (5)	58 (6)	55 (6)	10 (4)	13 (4)	19 (5)
C3B	0.0436 (11)	0.2690 (8)	0.5933 (8)	36 (5)	55 (6)	90 (8)	19 (5)	21 (5)	32 (6)
C4B	0.0897 (13)	0.3860 (9)	0.6339 (9)	56 (7)	72 (7)	83 (8)	40 (6)	24 (6)	42 (6)
C5B	0.2525 (12)	0.4475 (7)	0.6662 (7)	57 (6)	41 (5)	64 (6)	24 (5)	9 (5)	18 (5)
C6B	0.3710 (11)	0.3869 (7)	0.6623 (6)	46 (5)	42 (5)	41 (5)	10 (4)	9 (4)	17 (4)
C7B	0.6531 (10)	0.4238 (7)	0.7425 (6)	42 (5)	37 (5)	41 (5)	8 (4)	5 (4)	13 (4)
C8B	0.7687 (13)	0.5157 (7)	0.8160 (7)	65 (7)	34 (5)	50 (6)	0 (5)	7 (5)	11 (4)
C9B	0.8943 (12)	0.4949 (8)	0.8676 (7)	53 (6)	52 (6)	35 (5)	-4 (5)	-6 (4)	9 (4)
C10B	0.9102 (12)	0.3877 (9)	0.8523 (7)	58 (6)	58 (6)	47 (6)	8 (5)	2 (5)	15 (5)
C11B	0.7974 (11)	0.2948 (7)	0.7811 (6)	42 (5)	57 (6)	31 (5)	8 (4)	-2 (4)	17 (4)
C12B	0.6670 (10)	0.3174 (7)	0.7279 (6)	44 (5)	34 (5)	36 (5)	4 (4)	7 (4)	5 (4)

atom	<i>x</i>	<i>y</i>	<i>z</i>	atom	<i>x</i>	<i>y</i>	<i>z</i>
H2B <sup>a</sup>	0.129	0.126	0.568	H8B	0.758	0.595	0.829
H3B	-0.074	0.227	0.566	H9B	0.978	0.560	0.919
H4B	0.004	0.428	0.640	H10B	1.004	0.375	0.893
H5B	0.285	0.533	0.691	H11B	0.809	0.216	0.769

<sup>a</sup> For all hydrogen atoms  $U = 0.060 \text{ \AA}^2$ .

0.50 mm. An Enraf-Nonius automatic diffractometer was used with Mo K $\alpha$  radiation monochromatized by a dense graphite crystal assumed for all purposes to be ideally imperfect. Lattice constants and an orientation matrix were obtained from a least-squares fit of 25 centered reflections representing all parity groups and well distributed over reciprocal space. Final cell constants are presented in Table I, along with other pertinent information. The space group was determined to be either  $P1$  or  $P\bar{1}$ , on the basis of the Laue symmetry noted and the lack of any systematic absences. Intensities were measured by using the  $\theta$ - $2\theta$  scan technique, with the scan rate depending on the net count obtained in rapid prescans of each reflection. Two standard reflections were monitored after every 2 h of exposure time as a check of electronic reliability and crystal stability, and no abnormalities were found. A unique hemisphere of data was collected, according to the limits listed in Table I. In reduction of the data, Lorentz and polarization factors were applied, but no correction was made for absorption since the crystal was a reasonable approximation of a sphere. An acceptance criterion of  $I > 3\sigma(I)$  was used in determining the reflections to be used in least-squares refinement.

Normalized structure factor ( $|E|$ ) statistics indicated that the proper space group was the centrosymmetric one,  $P\bar{1}$ . Since there are four molecules per unit cell, this meant there have to be two independent monomers in the unique asymmetric unit. Interpretation of the Patterson map led to the positions of both of the independent tellurium atoms, and difference Fourier syntheses yielded all remaining non-hydrogen atoms. The usual sequence of isotropic and anisotropic

Table III. Intramolecular Bond Lengths ( $\text{\AA}$ )<sup>a</sup>

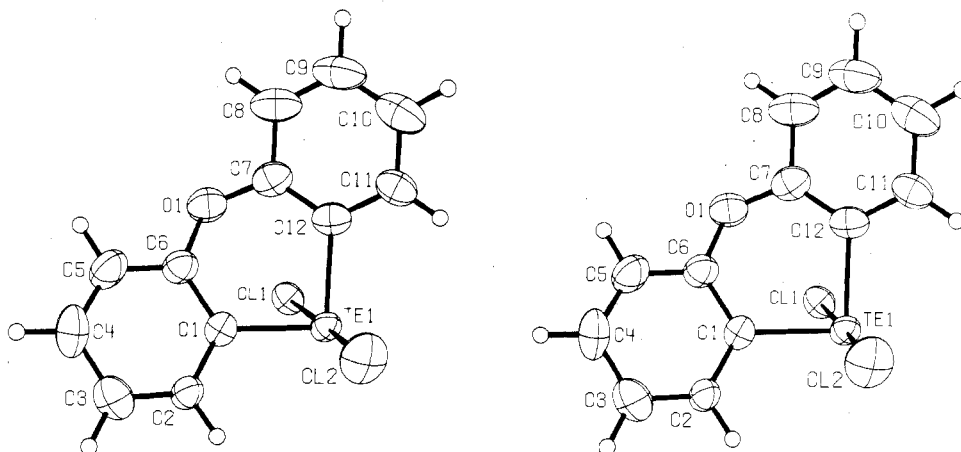
Te1-Cl1A	2.576 (3)	C4-C5	1.371 (13)
Te1-Cl2A	2.478 (3)	C5-C6	1.382 (15)
Te2-Cl1B	2.501 (3)	C6-O	1.364 (10)
Te2-Cl2B	2.563 (3)	O-C7	1.385 (12)
Te-C1	2.087 (9)	C7-C8	1.402 (11)
Te-Cl2	2.103 (7)	C7-C12	1.361 (14)
C1-C2	1.396 (10)	C8-C9	1.354 (16)
C1-C6	1.386 (11)	C9-C10	1.374 (18)
C2-C3	1.370 (14)	C10-C11	1.390 (12)
C3-C4	1.424 (14)	C11-C12	1.391 (14)

<sup>a</sup> Averaged over the two independent molecules, except for Te-Cl values. All hydrogens were fixed ideally at 1.00  $\text{\AA}$ .

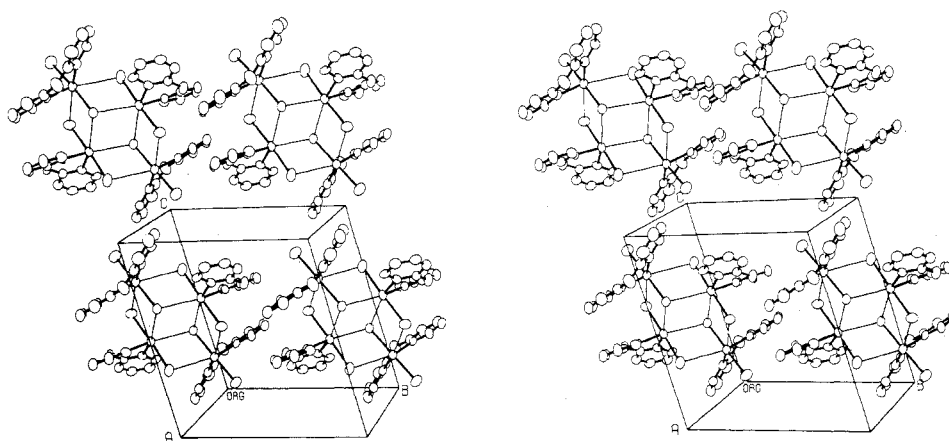
refinement was followed, after which the hydrogens were entered in ideally calculated positions. The hydrogens were ill-behaved, however, and finally had to be fixed at ideal values. After all shift/esd ratios were less than 0.1, the refinement converged to the agreement factors listed in Table I. The atomic scattering factors for the nonhydrogen atoms were computed from numerical Hartree-Fock wave functions;<sup>10</sup> for hydrogen those of Stewart, Davidson, and Simpson<sup>11</sup> were used.

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(11) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* 1965, **42**, 3175.



**Figure 1.** Stereoscopic view of the monomer showing the atom labeling scheme for each of the two independent molecules. The thermal ellipsoids are 50% equiprobability envelopes, with hydrogens of arbitrary size. Note that the coordination about Te is trigonal bipyramidal, with a lone electron pair in one of the three equatorial positions.



**Figure 2.** Stereoscopic packing diagram of the spatial arrangement of the tetramers about equivalent inversion centers at  $1/2, 0, 1/2$ . Note that the relative volumes of the thermal ellipsoids of the chlorines decrease as the number of secondary bonds to Te increases.

**Table IV.** Intramolecular Bond Angles (Deg)<sup>a</sup>

Cl1-Te-Cl2	176.8 (1)	C6-O-C7	124.5 (7)
Cl-Te-C12	90.7 (3)	O-C7-C8	114.3 (8)
Te-C1-C2	119.8 (6)	O-C7-C12	126.1 (6)
Te-C1-C6	120.5 (6)	C8-C7-C12	119.6 (9)
C2-C1-C6	119.7 (8)	C7-C8-C9	119.0 (10)
C1-C2-C3	121.2 (8)	C8-C9-C10	121.6 (8)
C2-C3-C4	118.2 (8)	C9-C10-C11	120.2 (10)
C3-C4-C5	120.5 (11)	C10-C11-C12	117.9 (9)
C4-C5-C6	120.5 (8)	C11-C12-C7	121.6 (7)
C5-C6-C1	119.9 (7)	C11-C12-Te	118.6 (6)
C5-C6-O	115.2 (7)	C7-C12-Te	119.7 (6)
C1-C6-O	124.9 (9)		

<sup>a</sup> Averaged over the two independent molecules. The hydrogens were all fixed at essentially trigonal angles about their respective carbons. The four averaged Cl-Te-C angles are 86.0 (3), 88.5 (3), 90.8 (3), and 91.2 (3)°.

The anomalous dispersion coefficients of Cromer and Liberman<sup>12</sup> were used for tellurium and chlorine. All calculations were made with the SHELX-76 series of programs.<sup>13</sup> No unusually high correlations were noted between any of the refined variables. Final positional and thermal parameters are given in Table II, and bond lengths, angles, and least-squares planes are given in Tables III-V on the basis of these positions. The atom labeling scheme is shown in Figure 1. The atoms in the two independent molecules are designated as A or B, respectively.

**Table V**

Least-Squares Planes			
plane 1:	Te1, Cl1A, Cl2A, O1	$0.2903x - 0.6787y - 0.6746z = -1.827$	
plane 2:	C1A-C6A	$0.0281x + 0.5231y - 0.8518z = -2.720$ largest out-of-plane distance = 0.019 (9) Å	
plane 3:	C7A-C12A	$-0.1116x + 0.8624y - 0.4937z = -1.766$ largest out-of-plane distance = 0.026 (9) Å	
plane 4:	Te2, Cl1B, Cl2B, O2	$-0.8778x - 0.0472y - 0.4767z = -6.423$	
plane 5:	C1B-C6B	$0.1630x + 0.3587y - 0.9191z = -7.044$ largest out-of-plane distance = 0.020 (11) Å	
plane 6:	C7B-C12B	$0.6118x + 0.3495y - 0.7096z = -4.124$ largest out-of-plane distance = 0.010 (9) Å	
Interplanar Angles (Deg)			
1,2	76.8	4,5	73.8
1,3	106.5	4,6	102.4
2,3	29.7	5,6	28.7

Te1 and O1 are in molecule A, while Te2 and O2 are in B. All hydrogens are labeled according to the atoms to which they are bonded.

### Discussion

In the solid state, the true molecular species found in the structure of phenoxatellurin 10,10-dichloride are discrete

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Table VI. Tetramer Bonding Parameters

Distances, Å			
Te1-C11A	2.576 (3)	C11A-Te1	2.576 (3)
Te1-C12A	2.478 (4)	C11A-Te2'	3.398 (4)
Te1-C11B	3.504 (4)	C11A-Te2	3.502 (4)
Te1-C12B'	3.368 (4)	C12A-Te1	2.478 (4)
Te2-C11B	2.500 (4)	C11B-Te2	2.500 (4)
Te2-C12B	2.563 (3)	C11B-Te1'	3.504 (4)
Te2-C11A'	3.398 (4)	C12B-Te2	2.563 (3)
Te2-C11A	3.502 (4)	C12B-Te1	3.368 (4)
Angles, Deg			
C12A-Te1-C11A	177.3 (1)	C11B-Te2-C12B	176.2 (1)
C12A-Te1-C12B	96.9 (1)	C11B-Te2-C11A'	80.9 (1)
C12A-Te1-C11B'	104.7 (1)	C11B-Te2-C11A	102.7 (1)
C11A-Te1-C12B	83.6 (1)	C12B-Te2-C11A'	99.6 (1)
C11A-Te1-C11B'	77.9 (1)	C12B-Te2-C11A	81.1 (1)
C12B-Te1-C11B'	91.6 (1)	C11A'-Te2-C11A	92.0 (1)
Te1-C11A-Te2'	100.9 (1)	Te2-C11B-Te1'	99.7 (1)
Te1-C11A-Te2	95.8 (1)	Te2-C12B-Te1	99.4 (1)
Te2'-C11A-Te2	88.0 (1)		

tetramers linked by intermolecular Te...Cl contacts. Each tetramer is situated about a crystallographic inversion center at  $(\frac{1}{2}, 0, \frac{1}{2})$ , as can be seen clearly in Figure 2, a stereoscopic packing diagram. Each Te atom has a distorted octahedral coordination consisting of two phenyl carbons, two primary-bonded chlorines, and two secondary-bonded chlorines. The bonding parameters for each of the two independently determined molecules are given in Table VI.

The intramolecular bond lengths and angles are not unusual for this type of compound.<sup>5,14-16</sup> There is always considerable strain at the oxygen, as can be seen by the internal angle of 124.5°. Concomitant distortions about C6 and C7 are also noted. Although the coordination about Te appears to be octahedral, each monomer unit is characteristically trigonal bipyramidal. This is seen from the comparison of the observed Te-C distances (average 2.09 Å) with the sum of the single-bond covalent radii for four-bonded Te (2.09 Å) vs. the sum for six-bonded Te (2.29 Å).<sup>17</sup> The Te-Cl bonds are somewhat weaker than normal (2.31 Å),<sup>17</sup> which would be expected for a structure with such a high degree of secondary bonding through the chlorine atoms. There are in fact three different types of chlorines in each tetramer—two with only one bond to Te, four with two bonds (one primary and one secondary), and two with three bonds (one primary, two secondary). From Table VI it can be seen that these have average bond lengths of 2.478 (4), 2.532 (4), and 2.576 (3) Å, respectively. Obviously, the less spread out the electron density on the chlorine, the shorter is the bond to tellurium. The secondary bonds range from 3.368 (4) to 3.504 (4) Å, considerably shorter than the sum of the van der Waals radii for these atoms (4.00 Å),<sup>18</sup> and in keeping with the values noted in previous structure determinations.<sup>3,19</sup>

It has long been recognized that molecules with an  $M_4X_4$  core can adopt two types of tetrameric arrangements—a "cubane" structure where each halogen contacts three different metals or a "step" structure where two halogens have three contacts and the remaining two have only two contacts.<sup>20</sup> The

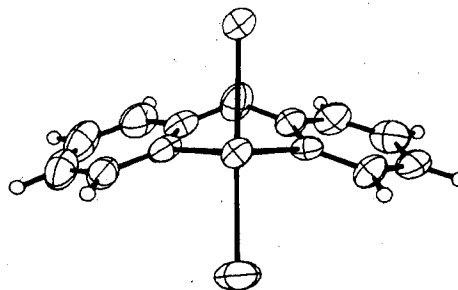


Figure 3. View of the monomer perpendicular to the Cl...Cl vector to illustrate the dihedral angle at the Te...O vector. The central ring is in the boat conformation.

step structure is the more stable when large halogens or bulky ligands are involved. The structure of  $TeCl_4$ , for example, is known to be in the compact "cubane" form.<sup>8</sup> In the present case, the tetrameric unit consists of an  $M_4X_6$  core which adopts a step structure with two additional sides formed by Te...Cl contacts. Other examples of tellurium compounds exhibiting such steplike tetramers are known,<sup>6,19</sup> but the majority of tellurium halide structures reported seem to be either dimers<sup>21</sup> or infinite pleated sheets.<sup>2-5,7,22</sup> Since the diiodo analogue of the present compound has been shown to form sheets rather than tetramers,<sup>2</sup> one would be tempted to assign this disparate behavior to the difference in size of the two halogens. Unfortunately, however, ( $\alpha$ -dimethyl)tellurium dichloride<sup>3</sup> also forms sheets rather than tetramers; so, such a simple answer as size alone must be discarded in favor of a more complex one which has yet to be determined.

Another parameter of interest in the present structural study is the fold angle of the two phenyl rings at the Te...O vector. This dihedral angle has previously been shown in related compounds to be a sensitive measure of the extent of delocalized bonding through the atoms bridging the two phenyl rings.<sup>23</sup> Figure 3 shows a view of the molecule perpendicular to the Cl-Te-Cl chain which clearly depicts this folding, which from Table V is seen to be an average of 29.2° from coplanarity, i.e., a dihedral angle of about 151°. This compares with the angle found in other 10,10-disubstituted phenoxatellurins: (i) bis(trifluoroacetate), 152°;<sup>14</sup> (ii) diiodide, 164°;<sup>5</sup> (iii) dinitrate, 175°.<sup>16</sup> For reference, the angle in the reduced, unsubstituted form, phenoxatellurin, is 145°.<sup>15</sup> The obvious questions raised are as follows: Why is the dinitrate almost flat and why does the diiodo analogue differ from the dichloride derivative by 13°? Although crystal packing forces may have some effect on the geometry of the ring system, there is no reason to suspect that they are a major contributor to the deformations noted. A fairly simple molecular orbital argument has been proposed to explain the folding along the Te...O vector in the reduced compound, i.e., to remove the extra electrons from the system and thus reduce the total energy;<sup>15</sup> however, similar arguments for the 10,10-disubstituted series appear to be inconsistent for different ligands. A more plausible explanation for the observed differences would seem to be one involving the electronegativities of the substituents, with the more electronegative groups producing a higher degree of back-donation of electron density to the tellurium. If one takes the order of electronegativities to be  $Cl > I > NO_3$ , then the magnitude of the deviations from planarity in the substituted phenoxatellurins would be predicted to be in the same order, as is found. Since the reduced, unsubstituted species has divalent Te, with two more electrons than the

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tetravalent disubstituted compounds, this would be expected to be at the high end of the series. This argument is, of course, predicated on the original MO reasoning of Meyer and co-workers mentioned above<sup>15</sup> but removes the need for separate MO schemes for each compound. Somewhat similar reasoning has been used to explain the differences in folding observed in the phenoxarsine series, but the emphasis was mainly on delocalization through the arsenic, and it was admitted that there was "no ready explanation" for the 20° difference between the Cl and S derivatives.<sup>22-25</sup>

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An interesting use of this theory might be the determination of relative electronegativities of unusual substituents, e.g., the observation that trifluoroacetate would be essentially equal to chlorine on the basis of the dihedral angle. One would predict that the difluoro compound would have an angle between 145 and 151°, and we hope to be able to investigate this in the near future.

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**Supplementary Material Available:** A listing of observed and calculated structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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## Synthesis and Structure of Two Crystalline Forms of (Cyclooctatetraene)thorium(IV) Dichloride-Bis(tetrahydrofuran)

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Th(C<sub>8</sub>H<sub>8</sub>)Cl<sub>2</sub>(OC<sub>4</sub>H<sub>8</sub>)<sub>2</sub> crystallizes in two modifications. The  $\alpha$  form, space group  $P2_1/n$ , has dimensions  $a = 8.589$  (4) Å,  $b = 27.222$  (10) Å,  $c = 7.950$  (4) Å,  $\beta = 96.92$  (5)°,  $Z = 4$ , and  $d_x = 1.99$  g/cm<sup>3</sup>. The  $\beta$  form, space group  $P2_1/c$ , has dimensions  $a = 13.036$  (6) Å,  $b = 11.601$  (6) Å,  $c = 24.598$  (10) Å,  $\beta = 102.90$  (5)°,  $Z = 8$ , and  $d_x = 2.02$  g/cm<sup>3</sup>. The  $\alpha$  form has one molecule in the asymmetric unit whereas the  $\beta$  form has two which are chemically equivalent but crystallographically different. The study thus yields three independent determinations of the same molecular structure. Thorium is bonded to the cyclooctatetraene ring, to two chlorine atoms, and to two oxygen atoms from the tetrahydrofuran moieties. Significant distances (averaged) are Th-Cl = 2.69 Å, Th-O = 2.57 Å, and Th-to-plane of C<sub>8</sub>H<sub>8</sub> = 2.02 Å.

### Introduction

Since the first synthesis of uranocene, bis( $\pi$ -cyclooctatetraene)uranium(IV),<sup>2</sup> a large number of related compounds have been prepared.<sup>3</sup> The bis(cyclooctatetraene) compounds of all the lower actinides are now known, including thorocene, bis( $\pi$ -cyclooctatetraene)thorium(IV).<sup>4</sup> X-ray crystal structures have been determined at Berkeley for several of these compounds.<sup>5</sup> All show the central metal atom in the center of two parallel planar eight-member rings.

We recently reported the preparation of mono(cyclooctatetraene)thorium(IV) dichloride and diborohydride.<sup>6</sup> In this paper we report the crystal structure of the dichloride which was isolated as the bis(tetrahydrofuran) compound, C<sub>8</sub>H<sub>8</sub>ThCl<sub>2</sub>·2C<sub>4</sub>H<sub>8</sub>O, **1**, by the reaction of thorocene with thorium tetrachloride in THF. Compound **1** is more soluble in THF than is thorocene itself.

### Experimental Section

**(Cyclooctatetraene)thorium Dichloride-Bis(tetrahydrofuran).** A suspension of 1.3 g (3.0 mmol) of thorocene and 1.7 g (4.5 mmol) of thorium tetrachloride in tetrahydrofuran (THF) was stirred at reflux under argon until the yellow color of thorocene disappeared (ca. 1 week). The mixture was degassed and taken into the glovebox, and the solid was separated by centrifugation. The THF-soluble portions were combined, and the solvent was removed by vacuum transfer. Crystals were grown from hot saturated THF solutions. Anal. Calcd for C<sub>16</sub>H<sub>24</sub>ThCl<sub>2</sub>O<sub>2</sub>: C, 34.86; H, 4.39; Cl, 12.86. Found: C, 34.65; H, 4.38; Cl, 12.22.

**X-ray Diffraction.** White crystals of the compounds, because of their extreme sensitivity to the atmosphere, were sealed inside thin-walled quartz capillaries for the X-ray experiments. Weissenberg

Table I. Summary of Crystal Data Intensity Collection and Least-Squares Refinement Statistics

	$\alpha$ -C <sub>8</sub> H <sub>8</sub> ThCl <sub>2</sub> ·(OC <sub>4</sub> H <sub>8</sub> ) <sub>2</sub>	$\beta$ -C <sub>8</sub> H <sub>8</sub> ThCl <sub>2</sub> ·(OC <sub>4</sub> H <sub>8</sub> ) <sub>2</sub>
fw	551.31	551.31
<i>a</i> , Å	8.589 (3)	13.036 (4)
<i>b</i> , Å	27.22 (2)	11.601 (3)
<i>c</i> , Å	7.950 (3)	24.598 (8)
$\beta$ , deg	96.92 (4)	102.90 (4)
<i>V</i> , Å <sup>3</sup>	1845	3626
space group	$P2_1/n$	$P2_1/c$
<i>Z</i>	4	8
<i>d</i> (calcd), g/cm <sup>3</sup>	1.985	2.020
color	white	white
cryst size, mm	parallelepiped, 0.1 × 0.2 × 0.3	0.15 × 0.15 × 0.3
cryst vol, mm <sup>3</sup>	0.007	0.007
$\mu$ , cm <sup>-1</sup>	288	293
<i>T</i> , °C	22	21
no. of scans (including stds)	5679	11 573
decay cor range	1.0-1.05	1.0-1.05
no. of unique data	2740	5390
no. data $F^2 > 3\sigma$ used in least-squares	2242	3914
extinction factor <i>k</i> ( $F_{\text{cor}} = (1 + kD)F_0$ )	$5 \times 10^{-7}$	$7 \times 10^{-7}$
ignorance factor, <i>p</i> , in weighting expression $w = [(\sigma(F^2))^2 + (pF^2)^2]^{-1}$	0.04	0.06
no. of variables in least squares	190	331
$R_w = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2}$	0.045	0.054
$R = \sum  \Delta F  / \sum  F_o $ ( $F^2 > 3\sigma$ )	0.036	0.045
<i>R</i> for all data	0.044	0.064
goodness of fit	1.24	1.16

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photography showed the material to be monoclinic, later designated as the  $\beta$  form. Upon investigating a different crystal on a Picker