

The Crystal Structure of Bisphenoxatelluronium Dinitrate, $C_{24}H_{16}O_9N_2Te_2$

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Bisphenoxatelluronium dinitrate is monoclinic, $P2_1/c$: $a = 11.638(4)$, $b = 28.266(8)$, $c = 8.546(3)$ Å, $\beta = 119.73(2)^\circ$, $z = 4$ at $t = 22^\circ$. All atoms including hydrogen were located. The two ring systems, I and II, are folded along their Te-O axes, 147° and 163° , respectively. The average ring bond distances are: Te-C = 2.091, C-C = 1.377, C-O = 1.370 Å. Each Te is bonded to one NO_3 group, Te1-ON1 = 2.485(5), Te2-ON4 = 2.393(4) Å, and an oxygen bridge connects the ring systems, Te1-OB = 1.966(4), Te2-OB = 2.001(4) Å, Te1-OB-Te2 = $125.0(2)^\circ$. The bond distances and angles of the structure are compared to those of related compounds.

Introduction.

In the course of experiments with phenoxatellurine, pt, it was observed (2) that mixing solutions of pt and its dinitrate, $pt(NO_3)_2$ in CH_2Cl_2 at room temperature gave a white precipitate. Since these materials also give purple products (2,3) when mixed together as solids or in solutions in CH_2Cl_2 at temperatures below -50° , it was thought at first that the room temperature product was a 1:1 complex between pt and $pt(NO_3)_2$. The determination of the structure of the white solid has shown that the room temperature product is bisphenoxatelluronium dinitrate, rather than a molecular complex. It appears that pt is oxidized by $pt(NO_3)_2$ at room temperature, and that the oxygen bridged compound which is produced has a limited solubility in dichloromethane. The study of this compound serves as a natural extension of the structural work described previously (4,5,6) in which the structures of pt, $pt(NO_3)_2$ and 10-acetylphenoxatellurine nitrate, $pt(Ac)NO_3$ have been determined.

EXPERIMENTAL

A small glass vial which contained $pt(NO_3)_2$ dissolved in dichloromethane was placed inside a beaker which was then carefully filled with a solution of pt in the same solvent. Crystals of $pt_2O(NO_3)_2$ grew on the rim of the vial.

A colorless crystal, $0.40 \times 0.15 \times 0.11$ (mm)³, was mounted on a pyrex fiber. Values of 2θ were measured manually at 22° with a Syntex diffractometer (graphite monochromatized $MoK\alpha$ radiation, $\lambda = 0.7107$ Å, $2\theta_{mon} = 12^\circ 15'$) for 16 general reflections. Least-squares refinement gave $a = 11.638(4)$, $b = 28.266(8)$, $c = 8.546(3)$ Å, $\beta = 119.73(2)^\circ$, $Z = 4$, space group $P2_1/c$. Intensities were collected automatically by scanning in 2θ (scan rate = 3° /min., scan range = 3° , $2\theta_{max} = 50^\circ$), and 2945 independent reflections were selected and corrected for Lorentz and polarization effects in the usual manner (4). An empirical absorption correction was obtained from a ϕ -scan at $\chi = 90^\circ$.

Structure Determination.

Coordinates of the two independent Te atoms were obtained from a three-dimensional Patterson synthesis, and least-squares refinements and difference Fourier

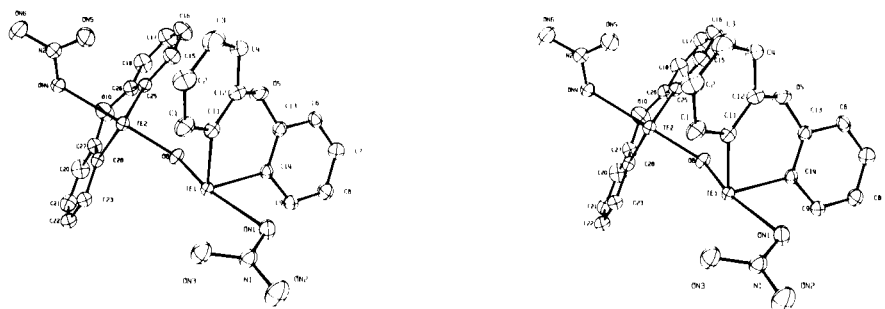


TABLE I
Atomic Coordinates and Standard Deviations ($\times 10^4$)

Atom	X/a (σ)	Y/b (σ)	Z/c (σ)	Atom	X/a (σ)	Y/b (σ)	Z/c (σ)
Te1	1707.0(4)	679.1(1)	725.0(5)	C16	3464(8)	2201(3)	6800(13)
Te2	332.3(4)	1310.2(1)	2950.9(5)	C17	2916(9)	2651(3)	6420(13)
OB	1299 (4)	1270 (1)	1564 (6)	C18	1676(9)	2718(3)	5113(14)
N1	1874 (5)	-341 (2)	-748 (7)	C20	-2179(8)	2501(3)	-117(12)
ON1	2661 (4)	7 (2)	-128 (6)	C21	-3076(8)	2305(3)	-1638(11)
ON2	2105 (6)	-658 (2)	-1517 (9)	C22	-3065(8)	1817(3)	-1947(10)
ON3	901 (5)	-357 (2)	-509 (7)	C23	-2068(7)	1547(3)	-634(9)
N2	-357 (5)	1270 (2)	6021 (7)	C25	1451(6)	1897(2)	4357(9)
ON4	-865 (4)	1476 (2)	4494 (6)	C26	911(7)	2349(3)	4023(10)
ON5	730 (5)	1081 (3)	6619 (8)	C27	-1176(7)	2221(3)	1268(10)
ON6	-971 (6)	1256 (3)	6810 (8)	C28	-1129(6)	1744(2)	986(9)
O5	4419 (5)	972 (2)	4444 (6)	H1	1290(66)	-107(27)	2856(94)
C1	2074 (7)	-5 (3)	3682 (9)	H2	2373(73)	-418(28)	5664(103)
C2	2667 (9)	-175 (3)	5422 (11)	H3	4029(73)	-52(30)	7542(108)
C3	3800 (9)	18 (3)	6748 (10)	H4	5108(70)	554(26)	7003(97)
C4	4373 (7)	403 (3)	6384 (9)	H6	6370(64)	1320(25)	4452(88)
C6	5664 (6)	1264 (3)	3207 (10)	H7	6593(64)	1548(26)	1801(89)
C7	5837 (6)	1362 (3)	1757 (10)	H8	5002(69)	1312(26)	-937(97)
C8	4893 (7)	1250 (3)	61 (10)	H9	3127(60)	930(25)	-1310(86)
C9	3725 (6)	1049 (3)	-234 (9)	H15	3063(68)	1536(27)	6093(95)
C11	2654 (6)	379 (2)	3308 (8)	H16	4480(74)	2148(30)	7319(105)
C12	3798 (7)	578 (2)	4656 (9)	H17	3383(77)	2812(30)	7300(110)
C13	4492 (6)	1060 (2)	2920 (8)	H18	1441(72)	2947(29)	4940(106)
C14	3507 (5)	960 (2)	1180 (8)	H20	-2087(72)	2762(29)	288(102)
O10	-345 (6)	2470 (2)	2794 (9)	H21	-3929(74)	2511(29)	-2689(108)
C15	2713 (7)	1828 (3)	5727 (11)	H22	-3894(70)	1628(28)	-3144(96)
				H23	-1964(63)	1204(25)	-800(87)

syntheses led to the location of all atoms, including hydrogen. For the final block-diagonal least-squares refinements, the data were empirically weighted by the function w , where $w = 1/\sigma^2$ and $\sigma = 2.62 - 0.026 |F_o|$ for $|F_o| < 35$ and $\sigma = 1.14 + 0.015 |F_o|$ for $|F_o| > 35$. The scattering factor for Te was corrected for anomalous dispersion (7). Each hydrogen was assigned an isotropic temperature factor, equal to that of the carbon atom to which it was bonded, and all other atoms were refined anisotropically (8). The structure was refined to final values of the discrepancy indices R_1 and R_2 :

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.032$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2} = 0.038.$$

The standard error in an observation of unit weight, Σ ,

was $\Sigma = 1.08$. The refinement was continued until all parameter shifts were less than 10% of their estimated standard deviations.

Results and Discussion.

Positional and thermal parameters are listed in Tables I and II, respectively, and principal bond distances and angles are given in Table III. Figure 1 is an ORTEP drawing of the molecule (9).

The two Te atoms of the structure are linked by an oxygen bridge: Te1-OB = 1.966(4), Te2-OB = 2.001(4) Å, Te1-OB-Te2 = 125.0(2)°. Both central rings are folded, but there is a pronounced difference in the angle of fold, which is 147° for ring system I and 163° for ring system II. In addition, I is folded away from its NO₃

TABLE II
Temperature Factors and Standard Deviations ($\times 10^4$)

	$\beta_{11}(\sigma)$	$\beta_{22}(\sigma)$	$\beta_{33}(\sigma)$	$\beta_{12}(\sigma)$	$\beta_{13}(\sigma)$	$\beta_{23}(\sigma)$
Te1	65.5(4)	8.0(1)	128.2(7)	-0.1(2)	52.0(8)	-0.7(3)
Te2	81.5(4)	8.1(1)	158.5(8)	-0.6(2)	67.0(9)	-2.0(3)
OB	113 (5)	7 (1)	194 (9)	1 (2)	100 (11)	-2 (3)
N1	99 (6)	9 (1)	180 (11)	-3 (3)	82 (13)	-7 (4)
ON1	83 (5)	13 (1)	247 (11)	-2 (3)	83 (12)	-10 (4)
ON2	191 (8)	11 (1)	395 (16)	-11 (4)	201 (20)	-25 (6)
ON3	110 (5)	15 (1)	282 (12)	-8 (3)	124 (14)	-14 (5)
N2	101 (6)	17 (1)	165 (11)	-5 (4)	70 (14)	4 (5)
ON4	91 (5)	14 (1)	166 (9)	3 (3)	66 (11)	-2 (4)
ON5	108 (6)	31 (1)	255 (13)	12 (5)	76 (15)	30 (7)
ON6	175 (8)	32 (1)	273 (14)	5 (5)	160 (18)	11 (7)
O5	139 (6)	17 (1)	157 (9)	-15 (4)	78 (12)	-18 (4)
C1	132 (9)	14 (1)	194 (15)	1 (5)	102 (19)	8 (7)
C2	193 (12)	14 (1)	224 (17)	1 (6)	120 (24)	15 (7)
C3	200 (12)	20 (2)	161 (15)	19 (7)	106 (23)	18 (7)
C4	132 (9)	19 (1)	128 (13)	9 (5)	64 (18)	1 (6)
C6	70 (7)	14 (1)	233 (16)	-2 (4)	46 (16)	-20 (7)
C7	84 (7)	13 (1)	252 (17)	-4 (4)	91 (18)	-5 (6)
C8	109 (8)	19 (1)	204 (15)	-3 (5)	93 (18)	3 (7)
C9	89 (7)	13 (1)	160 (13)	-2 (4)	60 (15)	0 (5)
C11	96 (7)	10 (1)	147 (12)	6 (4)	69 (15)	5 (5)
C12	108 (7)	13 (1)	152 (13)	1 (4)	70 (16)	-3 (5)
C13	83 (6)	11 (1)	166 (13)	-2 (4)	66 (15)	-7 (5)
C14	63 (6)	9 (1)	180 (12)	0 (3)	66 (14)	-6 (5)
O10	139 (7)	12 (1)	406 (17)	11 (4)	77 (18)	-20 (6)
C15	118 (9)	14 (1)	234 (17)	-2 (5)	66 (20)	-7 (7)
C16	120 (10)	18 (2)	325 (23)	-15 (6)	50 (24)	-17 (9)
C17	159 (11)	14 (1)	333 (23)	-14 (6)	91 (26)	-28 (9)
C18	151 (11)	10 (1)	367 (23)	-2 (5)	104 (26)	-17 (8)
C20	136 (10)	12 (1)	346 (22)	5 (5)	116 (25)	6 (8)
C21	146 (10)	18 (1)	238 (17)	10 (6)	103 (22)	16 (8)
C22	130 (9)	18 (1)	192 (15)	0 (6)	81 (20)	2 (7)
C23	110 (8)	13 (1)	168 (14)	0 (4)	67 (17)	0 (6)
C25	100 (7)	11 (1)	180 (13)	-5 (4)	82 (16)	-9 (5)
C26	104 (8)	11 (1)	246 (16)	-1 (4)	81 (18)	-13 (6)
C27	92 (7)	11 (1)	255 (16)	2 (4)	78 (18)	-2 (6)
C28	88 (7)	11 (1)	184 (13)	3 (4)	84 (16)	6 (5)

TABLE II (continued)

The isotropic temperature factors of hydrogen were held constant.

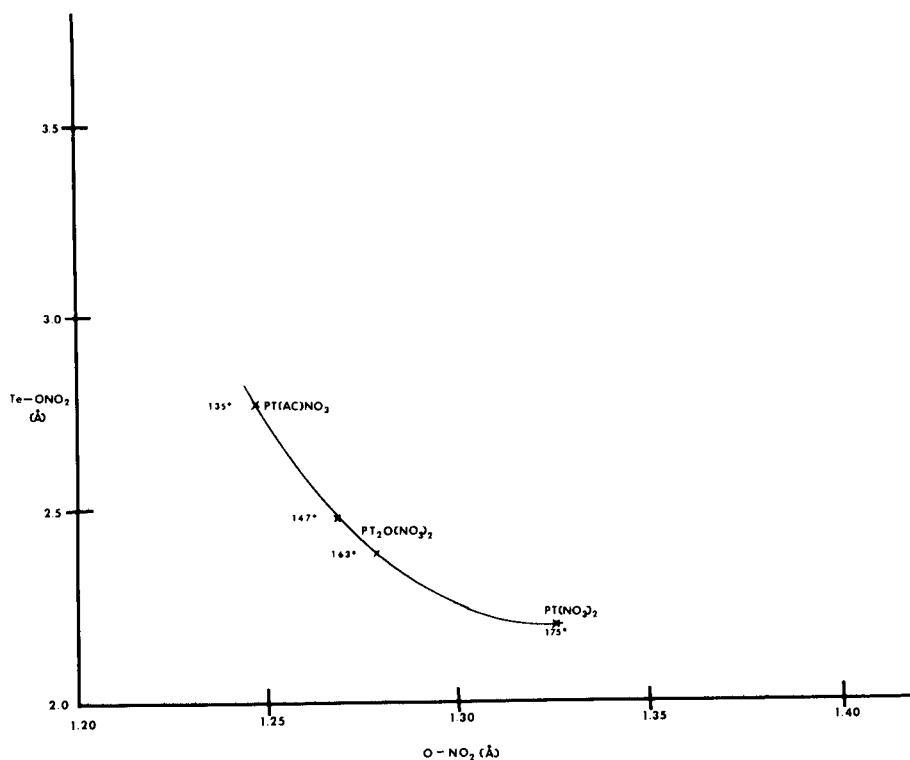
	B(\AA^2)		B		B
H1	4.9	H8	4.8	H18	5.5
H2	5.6	H9	3.8	H20	5.6
H3	5.9	H15	4.9	H21	5.7
H4	4.8	H16	6.1	H22	5.1
H6	4.2	H17	6.3	H23	4.2
H7	4.2				

TABLE III

Bond Distances, Bond Angles and Their Standard Deviations

Bond Distances (\AA)					
Te1-OB	1.966(4)	Te1-ON1	2.485(4)	Te1-C11	2.097(6)
Te1-C14	2.089(5)	Te2-OB	2.001(4)	Te2-ON4	2.393(4)
Te2-C25	2.084(6)	Te2-C28	2.094(6)	N1-ON1	1.267(6)
N1-ON2	1.218(7)	N1-ON3	1.247(6)	N2-ON4	1.276(7)
N2-ON5	1.227(8)	N2-ON6	1.202(8)	O5-C12	1.387(8)
O5-C13	1.370(7)	C1-C2	1.379(10)	C1-C11	1.396(9)
C2-C3	1.356(13)	C3-C4	1.389(13)	C4-C12	1.376(9)
C6-C7	1.379(10)	C6-C13	1.386(9)	C7-C8	1.352(10)
C8-C9	1.376(9)	C9-C14	1.376(8)	C11-C12	1.376(9)
C13-C14	1.383(8)	O10-C26	1.354(9)	O10-C27	1.370(9)
C15-C16	1.385(11)	C15-C25	1.364(10)	C16-C17	1.387(14)
C17-C18	1.330(13)	C18-C26	1.389(10)	C20-C21	1.319(12)
C20-C27	1.420(11)	C21-C22	1.404(12)	C22-C23	1.378(10)
C23-C28	1.386(9)	C25-C26	1.387(10)	C27-C28	1.376(9)
C1-H1	0.88 (7)	C2-H2	0.84 (8)	C3-H3	0.63 (8)
C4-H4	0.86 (7)	C6-H6	0.98 (6)	C7-H7	1.01 (6)
C8-H8	0.94 (7)	C9-H9	0.90 (6)	C15-H15	0.90 (7)
C16-H16	1.05 (7)	C17-H17	0.81 (8)	C18-H18	0.69 (8)
C20-H20	0.80 (8)	C21-H21	1.12 (8)	C22-H22	1.13 (7)
C23-H23	1.00 (7)				
Bond Angles ($^\circ$)					
Te1-OB-Te2	125.0(2)	OB-Te1-ON1	168.6(1)	OB-Te1-C14	90.6(2)
OB-Te1-C11	93.2(2)	ON1-Te1-C14	78.0(2)	ON1-Te1-C11	85.5(2)
OB-Te2-ON4	171.8(2)	OB-Te2-C28	91.7(2)	OB-Te2-C25	90.8(2)
ON4-Te2-C25	83.9(2)	ON4-Te2-C28	82.2(2)	Te1-ON1-N1	112.3(3)
ON1-N1-ON2	119.3(5)	ON2-N1-ON3	121.5(5)	ON1-N1-ON3	119.2(5)
Te2-ON4-N2	111.9(4)	ON4-N2-ON5	119.0(5)	ON5-N2-ON6	122.0(6)
ON4-N2-ON6	119.0(6)	C11-Te1-C14	90.2(2)	C11-C1-C2	118.5(7)
C1-C2-C3	121.3(7)	C2-C3-C4	120.3(6)	C3-C4-C12	119.4(7)
C4-C12-C11	120.3(6)	O5-C12-C11	124.7(6)	C12-O5-C13	123.6(5)

O5-C13-C14	125.1(5)	C6-C13-C14	119.6(6)	C7-C6-C13	119.6(6)
C6-C7-C8	120.9(6)	C7-C8-C9	119.7(6)	C8-C9-C14	120.7(6)
Te1-C14-C13	119.9(4)	Te1-C11-C12	120.0(5)	C25-Te2-C28	91.3(3)
Te2-C25-C26	121.6(5)	C15-C25-C26	119.6(6)	C16-C15-C25	121.1(7)
C15-C16-C17	118.4(7)	C16-C17-C18	120.7(7)	C17-C18-C26	121.5(7)
C18-C26-C25	118.7(7)	O10-C26-C25	126.6(6)	C26-O10-C27	126.1(5)
O10-C27-C28	126.7(6)	C20-C27-C28	119.2(7)	Te2-C28-C27	119.3(5)
C23-C28-C27	119.3(6)	C27-C20-C21	120.6(7)	C20-C21-C22	121.4(7)
C21-C22-C23	118.3(7)	C22-C23-C28	121.3(7)	C11-C1-H1	120 (5)
C2-C1-H1	121 (5)	C1-C2-H2	120 (5)	C3-C2-H2	118 (5)
C2-C3-H3	120 (7)	C4-C3-H3	120 (7)	C3-C4-H4	134 (5)
C12-C4-H4	107 (5)	C13-C6-H6	119 (4)	C7-C6-H6	122 (4)
C6-C7-H7	126 (4)	C8-C7-H7	113 (4)	C7-C9-H8	122 (4)
C9-C8-H8	118 (4)	C8-C9-H9	122 (4)	C14-C9-H9	116 (4)
C25-C15-H15	122 (4)	C16-C15-H15	116 (4)	C15-C16-H16	112 (4)
C17-C16-H16	121 (4)	C16-C17-H17	106 (6)	C18-C17-H17	130 (6)
C17-C18-H18	118 (6)	C26-C18-H18	121 (6)	C27-C20-H20	106 (5)
C21-C20-H20	133 (5)	C20-C21-H21	122 (4)	C22-C21-H21	117 (4)
C21-C22-H22	123 (4)	C23-C22-H22	118 (4)	C22-C23-H23	122 (4)
C28-C23-H23	116 (4)				



group, while II is folded toward its NO₃ group. There is little, if any, folding along the C11-C12, C13-C14 or C25-C26, C27-C28 axes. The average Te-C and C-ring oxygen distances are similar to those found in related molecules (4,5,6): Te1-C = 2.093, Te2-C = 2.089 Å, O5-C = 1.378, O10-C = 1.362 Å.

The distances between Te and the bonding oxygens of the NO₃ groups are intermediate between those obtained for pt(NO₃)₂ and pt(Ac)NO₃: Te-ON1 = 2.485(5), Te2-ON4 = 2.393(4) Å. In a similar manner, the structures of the NO₃ groups are also intermediate between those found in pt(NO₃)₂ and pt(Ac)NO₃: N1-ON1 = 1.267(6), N2-ON4 = 1.276(7) Å, ON2-N1-ON3 = 121.5(5), ON5-N2-ON6 = 122.0(6)°.

All C-C-C bond angles in the aromatic rings are close to 120°. The bond lengths C2-C3 = 1.36(1), C7-C8 = 1.35(1), C17-C18 = 1.33(1) and C20-C21 = 1.32(1) Å appeared to be shorter than anticipated. These results were viewed with scepticism, since no comparable shortening of bond lengths was observed in previous structures. For this study, data were collected only to 2θ = 50° rather than 2θ = 65° and it was thought that the origin of these discrepancies might lie here. (It should be pointed out that 2θ = 50° for MoK_α radiation gives more data than can be collected with CuK_α to 2θ = 133°). Several different refinement procedures were examined in order to test their effects upon these bond distances to uncover possible systematic errors.

(1) The φ-scan data were used to correct the intensities for absorption, and the block-diagonal least-squares refinement was used so as to treat interactions between (C2,C3), (C7,C8), (C17,C18) and (C20,C21). (In the usual block-diagonal method, the matrices employed are 9 x 9, whereas with this modification, they are expanded to 18 x 18 for the pairs of atoms selected as interacting). Generally, the changes in the bond distances were small: C2-C3 = 1.36, C7-C8 = 1.35, C17-C18 = 1.34 and C20-C21 = 1.32 Å.

(2) Apparent shrinkages in bond distances are known to occur when anisotropic thermal parameters are used in refinement (10). With absorption corrections included, and all atoms isotropic except Te, the following results were obtained: C2-C3 = 1.34, C7-C8 = 1.36, C17-C18 = 1.32 and C20-C21 = 1.31 Å.

(3) Systematic error in intensity measurements for high intensity reflections was considered to be a possibility. Refinement with data for which |F_o| < 20, with no absorption correction included and anisotropic betas gave C2-C3 = 1.33, C7-C8 = 1.39, C17-C18 = 1.36, C20-C21 = 1.31 Å. This use of approximately 50% of the available data did not seem to improve matters, but the variation in bond lengths increased.

(4) The data for sinθ/λ < 0.35, with absorption correc-

tions included and isotropic atoms, except Te, were refined and gave: C2-C3 = 1.39, C7-C8 = 1.38, C17-C18 = 1.37, C20-C21 = 1.33 Å. Again, probably because of the use of only 70% of the available data, the range in C-C distances became 1.33 to 1.43 Å, and the carbon oxygen distances became O10-C26 = 1.38, O10-C27 = 1.33 Å.

The net result of these tests seems to indicate that future data sets should be collected to 2θ = 65° although this entails the treatment of many more data than might have been thought necessary. Fortunately, none of the important distances which involve Te, O, NO₃, or the important angles such as the dihedral angles of the central ring seem to be affected seriously by the limitations of the present data set of 2954 reflections.

The systematic trends in some of the angles and distances that have been determined for pt(NO₃)₂, pt(Ac)NO₃ and pt₂O(NO₃)₂ are shown in Figure 2. There is a systematic relation between the Te-ONO₂ and TeO-NO₂ bond lengths, in which as one bond length increases, the other decreases. This variation also accompanies a regular change in the approach of the ring systems to planarity. There is also a trend towards shortening Te-C and C-ring oxygen distances as the central ring system becomes more nearly planar. These trends seem reasonable on the basis of increased participation of Te and O in the π-system of the central rings, but they also seem to argue for considerable covalent contributions in the bond between Te and O, points that were discussed in more detail in the preceding work (4,5,6). The existence of an oxygen bridge between Te atoms was unexpected, but recent work by McCullough (11) on the structure of the diiodide shows evidence for iodide bridges. The sum of covalent bond radii (12) for Te and O is 2.03 Å, and for tetrahedral covalent radii is 1.98 Å, so that the bridges appear to be normal Te-O bonds, although the Te1-O-Te2 angle is 125°. Oxygen is more electronegative than carbon, so that the approach of the ring systems toward planarity compared to pt(Ac)NO₃ is reasonable, and the effect of two Te atoms bonded to one O atom may be responsible for the fact that the rings are not completely planar as in pt(NO₃)₂.

All van der Waals' contact distances seem normal.

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