

The Crystal Structure of Phenoxatellurine Dinitrate, $C_{12}H_8O_7N_2Te$

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The crystal structure of phenoxatellurine dinitrate, $C_{12}H_8O_7N_2Te$, has been determined by x-ray diffractometer methods. The crystals are monoclinic, $C2/c$, $a = 12.916(3)$, $b = 14.050(5)$, $c = 7.532(2)$ Å; $\beta = 96.65(3)^\circ$ at $t = 22^\circ$. The molecule is nearly planar (175°), with the Te and O atoms of the central ring in special positions on the twofold symmetry axis. The bond distances for the central ring are: Te-C = 2.068(4) Å, C-O = 1.366(5), C-C = 1.388(6) with C-Te-C = $93.5(2)^\circ$ and C-O-C = $128.2(5)^\circ$. The bond distances and angles in the phenyl rings do not differ significantly from the normally accepted values of 1.40 Å and 120° . The two nitrate groups are close to Te and are related by the twofold axis of symmetry. The independent distances and angles are: Te-O1 = 2.201(3), O1-N = 1.325(5), N-O2 = 1.229(6), N-O3 = 1.204(6) Å, O2-N-O3 = $126.3(4)^\circ$, O1-N-O2 = $117.1(4)^\circ$, O1-N-O3 = $116.6(4)^\circ$. All hydrogen atoms were located at or near their calculated positions. The final R value for 1679 independent reflections was 0.031.

The planarity of the molecule is discussed qualitatively in terms of simple molecular orbital theory.

Introduction.

The structure of phenoxatellurine, pt, has been determined recently (2). One of the major goals of that study and of the present one is to achieve a better understanding of some of the physical and chemical properties of pt and of its derivatives as the oxidation number of Te is varied systematically. From a structural standpoint, we are interested in the effects that these changes in oxidation number have upon the bond distances and angles observed, especially since relatively little such information is available for organic tellurium compounds (3).

Many compounds of the type ptX_2 are known in which the oxidation number of Te is IV (3). The particular compound chosen for examination here, $pt(NO_3)_2$, was selected because it has the unusual property of forming an intensely colored purple product when crystals of it are rubbed together with crystals of pt itself (4). Thus, in

addition to serving the major purpose of giving information regarding the structural effects of changes in the oxidation number of Te, it also serves as a desirable preliminary to any examination of the structure of the colored complex. A partial study of $pt(NO_3)_2$ has been reported previously (5) by Kruse and McCullough.

EXPERIMENTAL

Single crystals of phenoxatellurine dinitrate were grown from methylene chloride in a Soxhlet extractor. A crystal, $0.40 \times 0.15 \times 0.11$ mm³, was mounted on a pyrex fiber and examined on a Buerger precession camera with $CuK\alpha$ radiation. The space group was ambiguous, systematic extinctions indicating either $C2/c$ or Cc . On the basis of the structure of phenoxatellurine (2), $C2/c$ was considered unlikely since it would require a C_2 central ring. It was therefore assumed initially that the space group was Cc . The crystal was aligned on a Syntex automated diffractometer. The unit cell parameters, which were determined

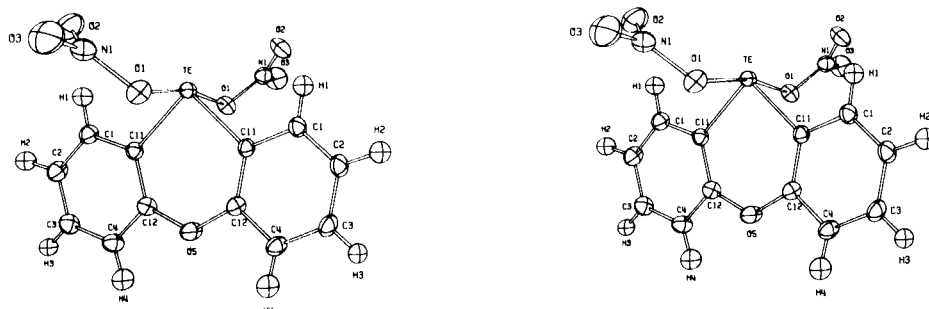


TABLE I
Atomic Coordinates and Standard Deviations ($\times 10^4$)

Atom	x/a(σ)	y/b(σ)	z/c(σ)
Te	0 (0)	1313.3(3)	2500.0(0)
O5	0 (0)	3717 (3)	2500.0(0)
N1	1815 (4)	879 (3)	5183 (6)
O1	1600 (3)	1478 (2)	3829 (5)
O2	1082 (4)	431 (3)	5670 (6)
O3	2711 (4)	842 (4)	5836 (7)
C1	-1008 (4)	2009 (4)	5639 (6)
C2	-1425 (4)	2652 (4)	6731 (7)
C3	-1361 (4)	3607 (4)	6385 (7)
C4	-888 (4)	3937 (4)	4957 (7)
C11	-521 (4)	2325 (3)	4184 (6)
C12	-457 (4)	3292 (3)	3842 (6)
H1	-1066 (46)	1336 (37)	5820 (74)
H2	-1785 (47)	2453 (39)	7807 (78)
H3	-1663 (47)	4031 (38)	7129 (69)
H4	-857 (49)	4582 (42)	4676 (79)

by least-squares refinement of 2θ values from 23 independent reflections, are: $a = 12.916(3)$, $b = 14.050(5)$, $c = 7.532(2)$ Å, $\beta = 96.65(3)^\circ$. Intensities were collected by scanning in 2θ (scan rate = $2^\circ/\text{min.}$, scan range = 3° , $2\theta_{\text{max}} = 65^\circ$), using $\text{MoK}\alpha$ radiation ($\lambda = 0.7107$ Å) monochromatized by reflection from the (002) plane of an oriented graphite crystal ($2\theta_{\text{mon}} = 12^\circ 15'$). Lorentz, polarization (6) and absorption corrections were applied to 1679 independent reflections in the manner described previously (2). The absorption correction was obtained from ϕ -scan data at $\chi = 90^\circ$. For these reflections, $I > 3\sigma(I)$, where $\sigma(I)$ was estimated from counting statistics.

Structure Determination.

A three-dimensional Patterson synthesis gave the y-coordinate of the tellurium atom. The x- and z-coordinates were assigned convenient values of 0.25 and 0.50 respectively and were not varied during subsequent refinement. Electron density syntheses (7) revealed the structure to be nearly planar and strongly suggested that the space group was C2/c. The tellurium atom and ring oxygen were then assigned to special positions (o, y, 0.25) on the twofold axis, and their x- and z-coordinates were held constant. A combination of least-squares refinements and Fourier syntheses led to the location of all atoms, including hydrogen. Block-diagonal least-squares refinement with unit

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

	$\beta_{11}(\sigma)$	$\beta_{22}(\sigma)$	$\beta_{33}(\sigma)$	$\beta_{12}(\sigma)$	$\beta_{13}(\sigma)$	$\beta_{23}(\sigma)$
Te	39.0(2)	30.0(2)	117.2(6)	0.0(0)	19.7(6)	0.0(0)
O5	70 (4)	37 (2)	195 (10)	0 (0)	65 (10)	0 (0)
N1	63 (3)	43 (2)	164 (8)	11 (4)	11 (8)	-3 (7)
O1	43 (2)	51 (2)	168 (7)	1 (3)	14 (6)	18 (6)
O2	91 (4)	60 (2)	218 (9)	-7 (4)	22 (10)	42 (8)
O3	69 (3)	81 (3)	295 (12)	16 (5)	-37 (10)	11 (10)
C1	55 (3)	44 (2)	133 (8)	5 (4)	27 (8)	6 (7)
C2	62 (4)	53 (3)	143 (9)	12 (5)	42 (10)	10 (8)
C3	57 (3)	51 (3)	149 (8)	10 (5)	33 (8)	-15 (8)
C4	53 (3)	40 (2)	179 (10)	2 (4)	34 (9)	-11 (8)
C11	41 (3)	38 (2)	111 (7)	3 (4)	15 (7)	-1 (6)
C12	38 (2)	39 (2)	146 (8)	0 (4)	19 (8)	-5 (7)

The temperature factors for hydrogen were isotropic.

	$B(\sigma)\text{Å}^2$
H1	3.4(7)
H2	3.7(8)
H3	3.0(4)
H4	4.2(9)

TABLE III

Bond Distances, Bond Angles and Their Standard Deviations

Bond Distances (Å)			
O1-Te	2.201(3)	C3-C4	1.378(7)
C11-Te	2.068(4)	C4-C12	1.394(6)
N1-O1	1.325(5)	C11-C12	1.388(6)
N1-O2	1.229(6)	C12-O5	1.366(5)
N1-O3	1.204(6)	C1-H1	0.96(5)
C1-C2	1.373(6)	C2-H2	1.02(5)
C1-C11	1.399(6)	C3-H3	0.93(5)
C2-C3	1.372(6)	C4-H4	0.93(5)
Bond Angles (°)			
C11-Te-O1	90.2(2)	Te-O1-N1	112.6(3)
O1-N1-O2	117.1(4)	O1-N1-O3	116.6(4)
O2-N1-O3	126.3(4)	Te-C11-C1	118.1(3)
Te-C11-C12	121.9(3)	C1-C11-C12	119.8(4)
C2-C1-C11	120.4(4)	C1-C2-C3	119.5(4)
C2-C3-C4	121.4(4)	C3-C4-C12	119.7(4)
C4-C12-C11	119.2(4)	C4-C12-O5	113.5(4)
O5-C12-C11	127.3(4)	O1-Te-O1'	168.0(2)
C12-O5-C12'	128.2(5)	C11-Te-C11'	93.5(2)
C2-C1-H1	121(3)	C11-C1-H1	118(3)
C1-C2-H2	123(3)	C3-C2-H2	118(3)
C2-C3-H3	118(3)	C4-C3-H3	120(3)
C3-C4-H4	123(3)	C12-C4-H4	118(3)

weights, anisotropic temperature factors for Te, O, N and C and isotropic temperature factors for H gave a final value of R_1 : $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.033$. For the final least-squares refinements, data were weighted by the empirical function, $w = 1/\sigma^2$: $\sigma = 1.88 + 0.005 |F_o|$ for $|F_o| > 35.0$; $\sigma = 3.06 - 0.030 |F_o|$ for $|F_o| \leq 35.0$, and corrections for anomalous dispersion were included (8). The final R values were $R_1 = 0.031$, $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / w |F_o|^2]^{1/2} = 0.037$; the error in an observation of unit weight, Σ , was $\Sigma = 0.900$. 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. Principal bond distances and angles are given in Table III. Figure 1 is an ORTEP drawing of the molecule.

The bond between Te and the NO₃ group is short and seems to be appreciably covalent. The Te-O1 distance is 2.201(3) Å, and the nitrate group is significantly distorted with N-O1 = 1.325(5) Å and O2-N-O3 = 126.3(4)°, while N-O2 = 1.229(6), N-O3 = 1.204(6) Å and O1-N-O2 = 117.1(4), O1-N-O3 = 116.6(4)°. A normal ionic NO₃ group would be expected to have equal bond distances, approximately 1.24 Å in length, and to have its bond angles equal to 120° (9). In primarily, not exclusively, covalent HNO₃, the distortion of the NO₃ moiety is very pronounced, with N-O1 = 1.405 Å and O2-N-O3 = 130° (10).

Due to the nearly planar central ring in pt(NO₃)₂, the distance Te-O5 = 3.378(5) Å is appreciably longer than the corresponding distance found for the boat conformation of pt, where Te-O5 = 3.251(5) Å (2). Very pronounced differences in the configurations of the ring systems are observed in the angles that involve O5, where O5-C12-C4 = 113.5(4)° and O5-C12-C11 = 127.3(4)° in pt(NO₃)₂, compared to corresponding (average) angles 116.1° and 122.7° in pt. The benzene rings appear normal in both structures, but pt(NO₃)₂ is very nearly planar. The close contact C11...O1' = 2.79 Å is probably responsible for the slight (5°) deformation observed. In contrast, the central ring in pt is folded at an angle of 138°, while the benzene rings make an angle of 145° with each other (2).

There are no abnormally short non-bonded contact distances between different molecules in the structure. Excluding hydrogen atoms, the shortest of these contacts is O5 ... O3' = 3.14 Å.

The planar structure of pt(NO₃)₂ may be explained on the basis of molecular orbital theory as was the folded configuration of phenoxatellurine (2). In the planar form, the pt moiety has the symmetry (C_{2v}) of acridine-like molecules (11). If the phenoxatellurine portion of the molecule exists (at least partially) as a doubly charged cation, two electrons would effectively be removed from the lowest antibonding orbital. In such a case, the planar configuration which would allow maximum π -overlap between C and O and between C and Te would be the most stable form. In addition, if the d_{z2} orbital of Te is used in bonding, it is possible to rationalize both the (apparently) partially covalent bonds between Te and NO₃, and because of the symmetry of d_{z2}, its lack of any major influence upon the acridine-like π -system. Regardless of the interpretation of course, there is a remarkable change in geometry associated with the transformation of Te(II) into Te(IV), and the discovery of such effects if they existed was one of the principal reasons for the study of these systems originally.

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