The Crystal Structure of 10-Acetonylphenoxatellurine Nitrate, $C_{15}H_{13}NO_5Te$

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The crystal structure of $C_{15}H_{13}NO_5Te$ was determined from X-ray diffractometer data. The unit cell is triclinic ($B\bar{1}$): a = 17.118(5), b = 7.402(2), c = 12.225(2) Å, α = 87.96(1), β = 93.31 (1), γ = 92.13(2)° at 22°C, Z = 4/cell, and the conventional R = 0.025 for 2497 independent reflections. The molecule is folded along the Te-ring oxygen axis (135°). The average Te-ring carbon distance is 2.101 Å, the Te-acetonyl carbon distance is 2.129 Å and the average C-ring oxygen distance is 1.388 Å. The acetonyl group and phenyl rings have normal distances and angles, and the nitrate group is nearly regular, with Te...ONO_2 = 2.775 Å. The coordination around Te is that of an extremely distorted trigonal bipyramid, with apical positions occupied by one ring carbon and the ONO_2 group (167.4°), and two axial positions occupied by the acetonyl carbon and the other ring carbon (94.6°). Coordinates of all hydrogen atoms were determined.

Introduction.

The structure of 10-acetonylphenoxatellurine nitrate (pt(Ac)NO_3) was determined in conjunction with other investigations of the effects of the oxidation state of Te on the dimensions and configurations of phenoxatellurine (pt) derivatives. The structures of pt (2) and of phenoxatellurine dinitrate (pt$(NO_3)_2$) (3) have already been described. Single crystals of pt(Ac)NO_3 were prepared during attempts to recrystallize pt$(NO_3)_2$ from acetone. According to a recent review (4), additions of organotellurium halides to the enol form of ketones are well documented. The analogous reactions of 10,10-disubstituted phenoxatellurine derivatives apparently have not been studied, and we are not aware of any reports in which organotellurium nitrates have afforded similar condensation reactions. It seems likely that the reaction will provide some interesting synthetic possibilities (5).

From a structural standpoint, pt(Ac)NO_3 is especially valuable because the dimensions of the acetonyl group are fairly close to those of the nitrate ion (6). Moreover, from single bond radii (7), the estimated $CH_3C(O)CH_2$-Te distance is 2.14 Å, and the Te-ONO_2 distance in pt$(NO_3)_2$ is 2.201 Å. Thus, pt(Ac)NO_3 and pt$(NO_3)_2$ afford the possibility of comparison of two compounds in which Te(IV) is present, and for which steric effects may be small.

EXPERIMENTAL

Crystals of pt(Ac)NO_3 were grown by evaporation of acetone solutions of phenoxatellurine dinitrate (pt$(NO_3)_2$). A colorless crystal 0.26 x 0.33 x 0.67 $(mm)^3$ was selected and mounted on a Pyrex fiber with ethereal varnish. Examination of the crystal on a Buerger precession camera (CuKα radiation) showed the crystal to be triclinic. The crystal was aligned on a Syntex automated

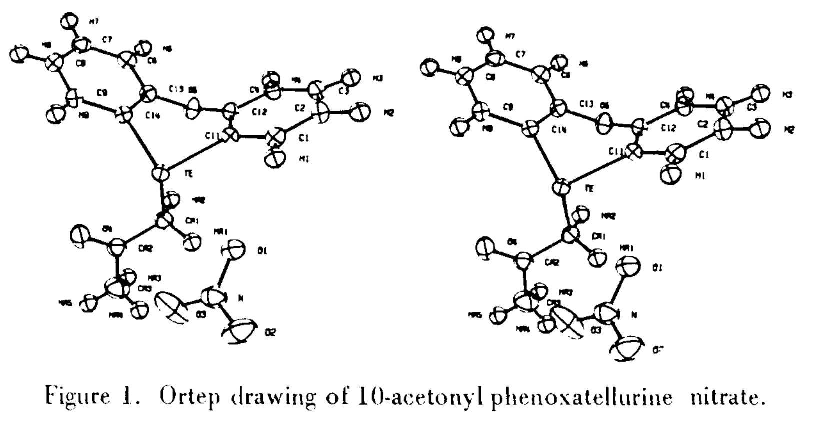

Figure 1. Ortep drawing of 10-acetonyl phenoxatellurine nitrate.

TABLE I

Atomic Coordinates and Standard Deviations (X10^4)

Atom	x/a(σ)	y/b(σ)	z/c(σ)	Atom	x/a(σ)	y/b(σ)	z/c(σ)
Te	573.4(2)	1575.9(4)	3367.5(2)	N	471(2)	2579(5)	6128(3)
O5	-128 (2)	3580 (4)	1165 (2)	O1	-25(2)	2359(5)	5352(3)
C1	-1208 (3)	1611 (7)	3480 (4)	O2	270(3)	2221(6)	7062(3)
C2	-1960 (3)	2014 (8)	3112 (4)	O3	1134(3)	3084(7)	5896(4)
C3	-2085 (3)	2974 (7)	2137 (5)	H1	-1083(26)	987(59)	4190(37)
C4	-1470 (3)	3489 (6)	1502 (4)	H2	-2465(24)	1604(55)	3586(35)
C6	562 (2)	2208 (6)	-174 (3)	H3	-2659(33)	3347(75)	1953(47)
C7	1118 (2)	1024 (6)	-462 (3)	H4	-1510(22)	4169(51)	893(32)
C8	1522 (2)	-5 (6)	328 (4)	H6	277(22)	2889(51)	-704(32)
C9	1374 (2)	133 (5)	1415 (3)	H7	1190(23)	910(54)	-1215(33)
C11	-583 (2)	2149 (5)	2852 (3)	H8	1943(27)	-798(64)	180(39)
C12	-716 (2)	3045 (5)	1853 (3)	H9	1650(23)	-498(54)	1962(34)
C13	418 (2)	2336 (5)	918 (3)	HA1	670(22)	4817(50)	4044(31)
C14	823 (2)	1324 (5)	1715 (3)	HA2	789(23)	4963(53)	2772(33)
CA1	956 (2)	4340 (5)	3447 (4)	HA3	1920(40)	7296(95)	3724(58)
CA2	1824 (2)	4379 (6)	3694 (3)	HA4	2019(41)	6143(94)	4776(59)
CA3	2180 (3)	6129 (8)	4074 (5)	HA5	2610(41)	6164(93)	3994(58)
O4	2199 (2)	3076 (5)	3584 (3)				

diffractometer (MoKα radiation), and values of 2θ were measured manually at 22° for 23 general reflections. Least-squares refinement gave lattice constants: a = 17.118(5), b = 7.402(2), c = 12.225(2) Å, and α = 87.96(1), β = 93.31(1), γ = 92.13(2)°. The unit cell was chosen as $B\bar{1}$, (B-centered) for convenience, Z = 4/cell. Intensities were collected automatically, scanning in 2θ (scan rate = 4°/min., scan range = 3°, $2\theta_{max}$ = 65°) using MoKα radiation (λ = 0.7107 Å) monochromatized by reflection from the (002) plane of an oriented graphite crystal (2θ mon = 12° 15′). The 2497 independent reflections were corrected for Lorentz, polarization and absorption effects in the usual manner (2). For these reflections $I > 3\sigma(I)$, where $\sigma(I)$ was estimated from counting statistics.

Structure Determination.

A three-dimensional Patterson map was calculated from 816 of the most intense reflections and the coordinates of Te were found. Lighter atoms were sought in electron density and difference electron density maps (interspersed with least-squares refinements) until all atoms except the methyl hydrogens were located. Block-diagonal least-squares (8) refinement of all 2497 reflections with unit weights, anisotropic temperature factors for Te, O and C atoms, and isotropic temperature factors for the H-atoms, gave R_1 = 0.050, where $R_1 = \Sigma|Fo\text{-}Fc|/\Sigma|Fo|$. The data were empirically weighted with $w = 1/\sigma^2$, where σ = 3.82-0.1511|Fo| for |Fo|<13.2 and σ = 1.86 + 0.0031 |Fo| for |Fo|>13.2. The scattering factor for Te was corrected for anomalous dispersion, and the structure was refined to give R_1 = 0.028, and a weighted agreement index R_2 = 0.036, where $R_2 = [\Sigma w(|Fo|\text{-}|Fc|)^2/\Sigma w|Fo|^2]^{1/2}$. The methyl H-atoms were now visible in difference Fourier syntheses. Their inclusion in least-squares refinements gave final values of R_1 = 0.025, R_2 = 0.029, and Σ = 0.80, where Σ is the standard error in an observation of unit weight. Refinements were continued until parameter shifts were less than 10% of their estimated standard deviations.

Results and Discussion.

Final coordinates and temperature factors are collected in Tables I and II, bond distances and angles in Table III, and an Ortep drawing of the molecule is shown in Figure 1.

The phenyl rings are regular and planar with the average values C-C = 1.381 Å, C-C-C = 120.0°. The dihedral angle between rings in 135° and there is no indication of additional folding along (C11-C12), (C13-C14). Within the acetonyl group, the average distances and angles are: C-C = 1.493 Å, C-O = 1.194 Å, C-C-O = 122.0° and C-C-C = 115.9°. All of these values appear to be normal (6). The NO_3 group is slightly distorted, with N-O1 = 1.246 Å and O2-N-O3 = 124.8°. The average C-O

TABLE II

Temperature Factors and Standard Deviations ($X10^4$)

	$\beta_{11}(\sigma)$	$\beta_{22}(\sigma)$	$\beta_{33}(\sigma)$	$\beta_{12}(\sigma)$	$\beta_{13}(\sigma)$	$\beta_{23}(\sigma)$
Te	29.4(1)	173.1(5)	52.8(2)	6.5(3)	0.4(2)	-4.8(4)
O5	40 (1)	197 (6)	85 (2)	26 (4)	7 (3)	21 (6)
C1	36 (2)	290 (11)	79 (4)	-5 (7)	9 (4)	-46 (10)
C2	30 (2)	374 (14)	111 (5)	-10 (8)	14 (5)	-69 (13)
C3	30 (2)	331 (13)	133 (5)	13 (7)	-5 (5)	-92 (14)
C4	38 (2)	247 (10)	95 (4)	29 (7)	-11 (4)	-32 (10)
C6	37 (2)	200 (8)	60 (3)	-2 (6)	-1 (3)	14 (8)
C7	38 (2)	244 (10)	55 (3)	-14 (6)	6 (4)	-21 (8)
C8	35 (2)	215 (9)	74 (3)	7 (6)	5 (4)	-32 (9)
C9	31 (1)	190 (8)	72 (3)	11 (6)	0 (3)	-10 (8)
C11	26 (1)	206 (8)	67 (3)	2 (5)	0 (3)	-29 (8)
C12	29 (1)	181 (8)	77 (3)	13 (5)	-1 (3)	-24 (8)
C13	32 (1)	159 (7)	64 (3)	3 (5)	2 (3)	0 (7)
C14	28 (1)	165 (7)	56 (3)	3 (5)	2 (3)	-9 (7)
CA1	36 (2)	167 (8)	80 (3)	8 (6)	-4 (4)	-18 (8)
CA2	38 (2)	230 (10)	63 (3)	-2 (6)	0 (4)	-9 (9)
CA3	53 (2)	300 (13)	136 (6)	-42 (9)	0 (6)	-46 (14)
O4	38 (1)	294 (8)	135 (4)	22 (5)	-3 (3)	-33 (9)
N	56 (2)	229 (8)	81 (3)	20 (6)	-14 (4)	-8 (8)
O1	47 (1)	369 (9)	70 (2)	-6 (6)	2 (3)	-40 (8)
O2	106 (3)	394 (11)	67 (3)	60 (9)	-8 (4)	-10 (9)
O3	58 (2)	595 (16)	176 (5)	-57 (9)	-41 (5)	88 (15)

The temperature factors of hydrogen were isotropic. Those of the methyl hydrogens were held constant. Standard deviations are given in parentheses.

	B(σ)Å^2		B(σ)		B
H1	5.6(11)	H7	4.5(9)	HA3	12.0
H2	4.8(10)	H8	6.3(12)	HA4	12.0
H3	8.6(15)	H9	4.5(9)	HA5	12.0
H4	4.0(9)	HA1	3.8(8)		
H6	4.0(9)	HA2	4.4(9)		

distance in the central ring is 1.388 Å and C12-O5-C13 = 119.2°.

The coordination around Te resembles a very badly distorted trigonal bipyramid. The apical positions are occupied by O1 and C14, Te-O1 = 2.775 Å, Te-C14 = 2.105 Å, O1-Te-C14 = 167.4°. The two Te-C axial bonds are Te-C11 = 2.097 Å, Te-CA1 = 2.129 Å, C11-Te-CA1 = 94.6°. The configuration is similar to, but even more distorted than, that found for α-dimethyltellurium dichloride (9). The extremely long Te-O1 bond, as well as the relatively minor deformation of the NO_3 group indicate that the Te...ONO_2 bond is primarily ionic in character. In diphenyliodonium nitrate (10), the closest I...ONO_2 distances are 2.768 Å and 2.877 Å, and the related N-O distance is 1.277 Å.

In descriptive terms, Te of the pt moiety has lost one electron to the NO_3 group, and has formed a third bond to the acetonyl group. The total number of electrons which are available for the formation of a perturbed acridine-like aromatic ring system is sixteen, as is the case for pt itself. The same MO arguments that apply to the pt structure apply here, with the result that a bent,

TABLE III

Bond Distances, Bond Angles and Their Standard Deviations

Bond Lengths (Å)

C11-Te	2.097(4)	C14-Te	2.105(4)	CA1-Te	2.129(4)
O1-Te	2.775(3)	C1-C2	1.379(7)	C1-C11	1.390(6)
C2-C3	1.376(8)	C3-C4	1.377(8)	C4-C12	1.384(6)
C11-C12	1.380(6)	C12-O5	1.386(5)	O5-C13	1.390(5)
C13-C14	1.379(5)	C6-C13	1.379(6)	C6-C7	1.386(6)
C7-C8	1.379(6)	C8-C9	1.375(6)	C9-C14	1.387(6)
CA1-CA2	1.498(6)	CA2-CA3	1.488(7)	CA2-O4	1.194(6)
N-O1	1.246(5)	N-O2	1.230(6)	N-O3	1.226(4)
C1-H1	0.99 (4)	C2-H2	1.10 (4)	C3-H3	1.04 (6)
C4-H4	0.88 (4)	C6-H6	0.93 (4)	C7-H7	0.94 (4)
C8-H8	0.97 (5)	C9-H9	0.92 (4)	CA1-HA1	0.99 (4)
CA1-HA2	0.96 (4)	CA3-HA3	1.05 (8)	CA3-HA4	0.92 (8)
CA3-HA5	0.75 (8)				

Bond Angles (°)

C11-Te-C14	88.9(1)	CA1-Te-O1	81.2(1)	C14-Te-CA1	95.1(2)
C11-Te-CA1	94.6(2)	C11-Te-O1	79.5(1)	C14-Te-O1	167.4(1)
C2-C1-C11	119.7(5)	C1-C2-C3	119.7(4)	C2-C3-C4	120.9(4)
C3-C4-C12	119.6(5)	C7-C6-C13	118.7(4)	C6-C7-C8	120.8(4)
C7-C8-C9	120.0(4)	C8-C9-C14	119.9(4)	Te-C11-C1	121.4(3)
Te-C11-C12	118.3(3)	C1-C11-C12	120.2(4)	C4-C12-C11	119.8(4)
C4-C12-O5	116.5(4)	C11-C12-O5	123.7(3)	C6-C13-O5	116.5(3)
C14-C13-O5	122.5(3)	C12-O5-C13	119.2(3)	C6-C13-C14	121.0(4)
C9-C14-C13	119.6(4)	Te-C14-C9	121.3(3)	Te-C14-C13	119.1(3)
Te-CA1-CA2	107.3(3)	CA1-CA2-CA3	115.9(4)	CA1-CA2-O4	121.2(4)
CA3-CA2-O4	122.9(4)	O1-N-O2	118.0(4)	O2-N-O3	124.8(4)
O1-N-O3	117.2(4)	C2-C1-H1	123 (3)	C11-C1-H1	117 (3)
C1-C2-H2	122 (2)	C3-C2-H2	119 (2)	C2-C3-H3	115 (3)
C4-C3-H3	124 (3)	C3-C4-H4	125 (3)	C12-C4-H4	115 (3)
C7-C6-H6	121 (2)	C13-C6-H6	120 (2)	C6-C7-H7	117 (2)
C8-C7-H7	122 (2)	C7-C8-H8	124 (3)	C9-C8-H8	116 (3)
C8-C9-H9	122 (3)	C14-C9-H9	118 (3)	Te-CA1-HA1	105 (2)
Te-CA1-HA2	109 (2)	HA1-CA1-HA2	108 (3)	CA2-CA3-HA3	115 (4)
CA2-CA3-HA4	102 (4)	CA2-CA3-HA5	110 (5)	HA3-CA3-HA4	101 (6)
HA3-CA3-HA5	110 (6)	HA4-CA3-HA5	118 (7)		

rather than planar configuration, is expected for the central ring. The bond distances and angles for the ring systems in pt and pt(Ac)NO_3 are remarkably similar, and the folded configuration of pt(Ac)NO_3 is in sharp contrast to the planar configuration of pt$(NO_3)_2$. The result seems of interest in that it shows the large changes in structure that can occur in the pt moiety with the replacement of an O_2NO group by another group of similar size and shape, $CH_3C(O)CH_2$.

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