Secondary Bonding. Part 9.[1] Crystal and Molecular Structures of μ-Oxo-bis[nitratodiphenyltellurium(IV)]–Diphenyltellurium(IV) Hydroxide Nitrate (1/1), Oxophenyltellurium(IV) Nitrate, and Diphenyltellurium(IV) Dinitrate

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The crystal and molecular structures of the title compounds have been determined from diffractometer data by the heavy-atom method. Crystals of $[\{Ph_2Te(NO_3)\}_2O]–Ph_2Te(NO_3)(OH)$ (1) are triclinic, space group $P\bar{1}$, with unit-cell dimensions (290 K) $a = 11.839(3)$, $b = 11.220(1)$, $c = 14.793(3)$ Å, $\alpha = 90.85(1)$, $\beta = 100.98(2)$, $\gamma = 99.28(2)°$, $Z = 2$, and for 5 577 observed reflections $[I/\sigma(I) \geqslant 3.0]$, $R = 0.022$. Crystals of $[PhTeO(NO_3)]_n$ (2) are triclinic, space group $P\bar{1}$, with unit-cell dimensions (290 K) $a = 11.555(5)$, $b = 5.350(2)$, $c = 14.987(3)$ Å, $\alpha = 94.89(3)$, $\beta = 110.68(3)$, $\gamma = 106.07(3)°$, $Z = 4$, and for 2 465 observed reflections, $R = 0.026$. Crystals of $Ph_2Te(NO_3)_2$ (3) are monoclinic, space group $C2/c$, with unit-cell dimensions (233 K) $a = 17.929(6)$, $b = 7.100(2)$, $c = 11.193(2)$ Å, $\beta = 94.38(2)°$, $Z = 4$, and for 1 100 observed reflections, $R = 0.031$. All three compounds contain four-co-ordinate pseudo-trigonal-bipyramidal tellurium atoms each with the lone pair in the vacant equatorial position. Compound (3) is essentially monomeric, while in (1) the component molecules are linked by bridging nitrate groups and (2) is polymeric. All contain weak secondary bonds Te · · · O (2.862—3.514 Å), Te–C 2.094—2.120, Te–OH in (1) 1.953(3), Te–O(bridge) 1.887—2.015, and Te–O(NO_3) 2.171—2.533 Å.

THE structures of a basic tellurium(IV) nitrate and a sulphate have been determined,[2] but for organotellurium(IV) derivatives very few oxy-salts have been examined. By comparison with organoiodine(III) compounds, these oxy-salts are likely to show interesting intra- and inter-molecular secondary bonding. The phenyliodine nitrate and acetate were found to form forked secondary bonds, rather than the linear C–I · · · X systems found with X = halide. Potentially, three series of phenyltellurium(IV) salts exist: $PhTeX_3$, Ph_2TeX_2, and Ph_3TeX. Within the first two, the possibility exists of obtaining basic (oxygen-bridged) species, as well as simple salts: in the iodine system, it has proved impossible to obtain the nitrate other than as dinitrato-μ-oxo-diphenyldiiodine(III).[3] We describe here the basic nitrate in the $PhTeX_3$ series, $[PhTeO(NO_3)]_n$ (2), the simple $Ph_2Te(NO_3)_2$ (3), and the basic species (1), readily formed from (3) by atmospheric hydrolysis, which proves to be a complicated adduct of a μ-oxo-nitrate and a hydroxy-nitrate, $[\{Ph_2Te(NO_3)\}_2O]–Ph_2Te(NO_3)(OH)$.

EXPERIMENTAL

Compound (1) was prepared during an attempt to prepare (3) by treating Ph_2TeCl_2 with a slight excess of $AgNO_3$ in refluxing benzene. Removal of AgCl and slow evaporation in air gave colourless well formed crystals of (1) (Found: C, 40.1; H, 2.95; N, 3.40%). Crystals that exhibited the same i.r. spectra as (1) were prepared by dissolving Ph_2TeO in dilute nitric acid and evaporating in air. Compound (1) was expected to be $[Ph_2Te(NO_3)]_2O$ but crystal-structure analysis showed the following stoicheiometry to be correct: $[Ph_2Te(NO_3)]_2O–Ph_2Te(NO_3)(OH)$ ($C_{36}H_{31}N_3O_{11}Te_3$ requires C, 40.6; H, 2.95; N, 3.95%). Compound (2) was prepared by leaving a suspension of diphenyl ditelluride in hot dilute nitric acid until a colourless

TABLE 1

Crystal data

	(1)	(2)	(3)
Formula	$C_{36}H_{31}N_3O_{11}Te_3$	$(C_6H_5NO_4Te)_n$	$C_{12}H_{10}N_2O_6Te$
M	1 064.5	282.7	405.8
Absences	None	None	hkl: $h + k \neq 2n$ $h0l$: $l \neq 2n$ ($h \neq 2n$) $0k0$: $k \neq 2n$
Space group (assumed)	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	11.839(3)	11.555(5)	17.929(6)
b/Å	11.220(1)	5.350(2)	7.100(2)
c/Å	14.793(3)	14.987(3)	11.193(2)
α/°	90.85(1)	94.89(3)	
β/°	100.98(2)	110.68(3)	94.38(2)
γ/°	99.28(2)	106.07(3)	
U/Å^3	1 901.8(6)	815.4(4)	1 420.7(6)
Z	2	4	4
D_c/g cm^{-3}	1.89	2.30	1.90
D_m/g cm^{-3}	1.92	2.28	—
$F(000)$	1 024	528	784
μ/cm^{-1}	23.5	36.3	21.2
Observed reflections $[I/\sigma(I) > 3.0]$	5 577	2 465	1 100
R(final)	0.022	0.026	0.031

solution was obtained; on cooling, bunches of needle-like crystals of (2) formed. Compound (2) can also be prepared by treating ' PhTeOCl ' (obtained from the hydrolysis of $PhTeCl_3$) with a slight excess of aqueous $AgNO_3$; filtration

TABLE 2

Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
(*a*) For (1)			
Te(1)	4 276.8(3)	4 462.6(2)	8 147.7(2)
Te(2)	943.2(2)	24.4(2)	8 655.7(1)
Te(3)	−1 425.8(2)	1 004.8(2)	7 226.3(1)
O(1)	2 552(2)	−207(3)	9 909(2)
O(2)	1 293(3)	−67(4)	10 766(2)
O(3)	3 062(3)	−130(4)	11 387(2)
O(4)	−3 154(3)	1 888(3)	6 555(2)
O(5)	−4 278(4)	3 148(4)	6 720(3)
O(6)	−2 588(5)	3 349(4)	7 558(4)
O(7)	−144(2)	57(2)	7 461(2)
O(8)	2 080(3)	3 978(3)	7 981(2)
O(9)	2 415(3)	2 843(3)	9 138(3)
O(10)	677(3)	2 710(3)	8 356(2)
O(11)	5 901(3)	5 121(3)	8 124(3)
N(1)	2 298(3)	−131(3)	10 706(2)
N(2)	−3 339(4)	2 816(4)	6 956(3)
N(3)	1 717(3)	3 165(3)	8 503(2)
C(1)	2 321(3)	143(3)	7 916(2)
C(2)	2 279(4)	892(4)	7 184(3)
C(3)	3 190(5)	1 034(5)	6 701(4)
C(4)	4 114(4)	419(5)	6 950(4)
C(5)	4 150(4)	−325(5)	7 680(4)
C(6)	3 255(4)	−473(4)	8 180(3)
C(7)	512(3)	−1 879(3)	8 627(3)
C(8)	736(4)	−2 580(4)	7 932(3)
C(9)	360(5)	−3 819(4)	7 889(4)
C(10)	−226(6)	−4 339(4)	8 532(5)
C(11)	−449(6)	−3 640(5)	9 223(5)
C(12)	−67(5)	−2 405(4)	9 287(4)
C(13)	−2 542(3)	−560(3)	6 581(3)
C(14)	−2 426(4)	−1 630(4)	7 021(3)
C(15)	−3 189(5)	−2 671(4)	6 677(4)
C(16)	−4 030(4)	−2 650(5)	5 904(4)
C(17)	−4 142(4)	−1 598(5)	5 463(3)
C(18)	−3 394(4)	−536(4)	5 801(3)
C(19)	−788(3)	1 755(3)	6 086(2)
C(20)	−207(4)	2 944(4)	6 218(3)
C(21)	346(4)	3 433(5)	5 520(4)
C(22)	305(4)	2 773(5)	4 728(4)
C(23)	−289(5)	1 605(5)	4 597(3)
C(24)	−837(4)	1 086(4)	5 280(3)
C(25)	3 628(4)	5 293(4)	6 938(3)
C(26)	3 559(4)	4 693(4)	6 101(3)
C(27)	3 151(4)	5 224(5)	5 291(3)
C(28)	2 802(4)	6 339(5)	5 329(4)
C(29)	2 877(5)	6 925(5)	6 158(4)
C(30)	3 285(5)	6 417(5)	6 970(3)
C(31)	4 230(4)	5 873(4)	9 092(3)
C(32)	5 162(4)	6 820(5)	9 264(4)
C(33)	5 145(5)	7 750(5)	9 883(4)
C(34)	4 243(5)	7 744(5)	10 336(4)
C(35)	3 313(5)	6 808(5)	10 152(4)
C(36)	3 319(5)	5 862(5)	9 546(4)
H(2)	1 672	1 401	7 003
H(3)	3 136	1 567	6 101
H(4)	4 774	574	6 604
H(5)	4 884	−796	7 898
H(6)	3 222	−1 047	8 700
H(8)	1 134	−2 210	7 490
H(9)	550	−4 328	7 408
H(10)	−499	−5 327	8 505
H(11)	−924	−4 099	9 700
H(12)	−277	−1 843	9 820
H(14)	−1 753	−1 620	7 594
H(15)	−3 141	−3 395	6 834
H(16)	−4 628	−3 461	5 637
H(17)	−4 801	−1 646	4 888
H(18)	−3 447	268	5 471

TABLE 2 (*continued*)

Atom	*x*	*y*	*z*
(*a*) For (1) (*continued*)			
H(20)	−197	3 473	6 742
H(21)	700	4 275	5 564
H(22)	732	3 107	4 250
H(23)	−316	1 076	3 972
H(24)	−1 249	204	5 176
H(26)	3 734	3 794	6 089
H(27)	3 094	4 742	4 673
H(28)	2 463	6 684	4 734
H(29)	2 583	7 746	6 115
H(30)	3 344	6 812	7 625
H(32)	5 862	6 838	8 894
H(33)	5 839	8 464	10 061
H(34)	4 252	8 409	10 877
H(35)	2 587	6 837	10 483
H(36)	2 724	5 263	9 443
(*b*) For (2)			
Te(1)	4 250.1(3)	2 767.5(6)	6 437.5(2)
Te(2)	3 833.7(3)	761.8(6)	2 429.1(2)
C(11)	2 362(5)	1 653(11)	6 429(4)
C(12)	1 508(6)	−892(13)	5 976(5)
C(13)	263(6)	−1 620(13)	5 991(5)
C(14)	−113(6)	160(14)	6 437(5)
C(15)	753(6)	2 733(14)	6 887(5)
C(16)	1 990(6)	3 470(12)	6 868(5)
C(21)	3 195(6)	192(12)	911(4)
C(22)	2 862(31)	2 060(51)	446(12)
C(23)	2 450(32)	1 684(54)	−577(13)
C(24)	2 342(10)	−465(19)	−1 070(6)
C(25)	2 600(25)	−2 556(37)	−655(10)
C(26)	3 067(21)	−2 176(29)	367(11)
C(221)	1 959(17)	330(41)	405(12)
C(231)	1 593(17)	108(41)	−602(12)
C(251)	3 548(23)	−482(62)	−513(13)
C(261)	6 029(19)	222(48)	9 512(11)
O(11)	3 678(4)	6 348(7)	5 662(3)
O(12)	3 524(4)	4 108(8)	4 326(3)
O(13)	3 391(5)	8 055(10)	4 388(3)
O(14)	4 718(3)	489(6)	7 393(2)
O(21)	2 910(3)	−3 728(7)	2 202(3)
O(22)	1 149(5)	−6 533(11)	2 191(4)
O(23)	1 211(5)	−2 531(10)	2 013(3)
O(24)	4 906(3)	5 678(6)	7 487(2)
N(11)	3 508(4)	6 132(8)	4 754(3)
N(21)	1 608(5)	−4 316(10)	2 157(3)
H(12)	1 601	−2 233	5 500
H(13)	−447	−3 358	5 500
H(14)	−970	−425	6 500
H(15)	342	4 049	7 074
H(16)	2 618	5 171	7 250
H(22)	7 278	6 504	9 209
H(23)	7 790	6 940	10 921
H(24)	7 938	10 658	11 769
H(25)	7 454	14 194	11 044
H(26)	6 703	13 541	9 309
H(221)	8 036	−1 679	9 119
H(231)	8 681	−1 295	11 060
H(251)	6 451	−873	10 931
H(261)	5 661	8 591	8 993
(*c*) For (3)			
Te	0.0	2 178.5(7)	2 500.0
C(1)	893(3)	4 073(8)	2 870(5)
C(2)	984(3)	5 579(9)	2 117(5)
C(3)	1 604(3)	6 712(10)	2 333(6)
C(4)	2 117(3)	6 349(10)	3 287(6)
C(5)	2 019(3)	4 856(10)	4 035(6)
C(6)	1 402(3)	3 681(10)	3 822(5)
O(1)	117(2)	2 583(5)	601(3)
O(2)	626(3)	1 280(7)	−878(4)
O(3)	1 086(3)	743(7)	931(4)
N(1)	641(3)	1 480(7)	198(4)
H(2)	663(35)	5 851(85)	1 568(56)
H(3)	1 717(46)	7 650(114)	1 822(76)
H(4)	2 528(44)	7 064(106)	3 401(65)
H(5)	2 369(40)	4 612(98)	4 666(63)
H(6)	1 287(40)	2 708(107)	4 309(69)

TABLE 3

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) For (1)

Te(1)–O(11)	1.953(3)	Te(2)–O(7)	1.983(2)	Te(3)–O(7)	1.971(3)	O(11)–Te(1)–O(8)	168.1(1)	O(7)–Te(2)–O(1)	166.9(1)	O(7)–Te(3)–O(4)	165.3(1)
Te(1)–O(8)	2.533(3)	Te(2)–O(1)	2.441(2)	Te(3)–O(4)	2.463(3)	O(11)–Te(1)–C(25)	93.5(2)	O(7)–Te(2)–C(1)	88.1(1)	O(7)–Te(3)–C(13)	88.7(1)
Te(1)–C(25)	2.102(4)	Te(2)–C(1)	2.120(4)	Te(3)–C(13)	2.112(3)	O(11)–Te(1)–C(31)	90.0(2)	O(7)–Te(2)–C(7)	90.3(1)	O(7)–Te(3)–C(19)	90.1(1)
Te(1)–C(31)	2.110(4)	Te(2)–C(7)	2.113(3)	Te(3)–C(19)	2.108(4)	O(8)–Te(1)–C(25)	75.6(1)	O(1)–Te(2)–C(1)	80.2(1)	O(4)–Te(3)–C(13)	79.9(1)
Te(1) · · · O(9)	3.214(4)	Te(2) · · · O(2)	3.076(3)	Te(3) · · · O(6)	3.231(6)	O(8)–Te(1)–C(31)	86.7(1)	O(1)–Te(2)–C(7)	85.6(1)	O(4)–Te(3)–C(19)	82.9(1)
Te(1) · · · O(5′)	3.415(5)	Te(2) · · · O(9)	3.351(3)	Te(3) · · · O(10)	3.072(3)	C(25)–Te(1)–C(31)	97.4(2)	C(1)–Te(2)–C(7)	98.0(2)	C(13)–Te(3)–C(19)	100.2(1)
		Te(2) · · · O(10)	3.109(3)	Te(3) · · · O(2′)	3.149(3)						
		Te(2) · · · O(2′)	2.940(3)	Te(3) · · · O(3′)	3.143(4)						
						O(8)–N(3)–O(9)	119.4(4)	O(1)–N(1)–O(2)	119.1(3)	O(4)–N(2)–O(5)	118.7(4)
						O(8)–N(3)–O(10)	119.5(3)	O(1)–N(1)–O(3)	119.2(3)	O(4)–N(2)–O(6)	119.4(5)
						O(9)–N(3)–O(10)	121.0(4)	O(2)–N(1)–O(3)	121.7(4)	O(5)–N(2)–O(6)	121.9(5)
						Te(1)–O(8)–N(3)	114.9(2)	Te(2)–O(1)–N(1)	113.3(2)	Te(3)–O(4)–N(2)	118.2(2)
						Te(1)–C(25)–C(26)	118.2(3)	Te(2)–C(1)–C(2)	117.2(3)	Te(3)–C(13)–C(14)	115.8(3)
						Te(1)–C(25)–C(30)	121.4(3)	Te(2)–C(1)–C(6)	121.4(3)	Te(3)–C(13)–C(18)	123.3(3)
N(3)–O(8)	1.278(7)	N(1)–O(1)	1.276(4)	N(2)–O(4)	1.260(5)	Te(1)–C(31)–C(32)	118.3(4)	Te(2)–C(7)–C(8)	120.6(3)	Te(3)–C(19)–C(20)	115.9(3)
N(3)–O(9)	1.227(5)	N(1)–O(2)	1.224(5)	N(2)–O(5)	1.219(6)	Te(1)–C(31)–C(36)	121.9(3)	Te(2)–C(7)–C(12)	118.7(3)	Te(3)–C(19)–C(24)	122.8(3)
N(3)–O(10)	1.231(5)	N(1)–O(3)	1.219(4)	N(2)–O(6)	1.206(6)			Te(2)–O(7)–Te(3)	125.5(1)		
C(25)–C(26)	1.382(6)	C(1)–C(2)	1.379(6)	C(13)–C(14)	1.388(6)	C(30)–C(25)–C(26)	120.5(4)	C(6)–C(1)–C(2)	121.3(4)	C(18)–C(13)–C(14)	120.8(4)
C(26)–C(27)	1.385(7)	C(2)–C(3)	1.393(7)	C(14)–C(15)	1.380(6)	C(25)–C(26)–C(27)	119.6(5)	C(1)–C(2)–C(3)	119.1(4)	C(13)–C(14)–C(15)	118.8(4)
C(27)–C(28)	1.383(9)	C(3)–C(4)	1.381(7)	C(15)–C(16)	1.368(7)	C(26)–C(27)–C(28)	119.6(5)	C(2)–C(3)–C(4)	120.1(5)	C(14)–C(15)–C(16)	120.5(5)
C(28)–C(29)	1.363(8)	C(4)–C(5)	1.373(8)	C(16)–C(17)	1.371(8)	C(27)–C(28)–C(29)	120.4(5)	C(3)–C(4)–C(5)	120.4(5)	C(15)–C(16)–C(17)	120.9(4)
C(29)–C(30)	1.375(8)	C(5)–C(6)	1.393(7)	C(17)–C(18)	1.388(6)	C(28)–C(29)–C(30)	120.9(6)	C(4)–C(5)–C(6)	120.6(5)	C(16)–C(17)–C(18)	119.8(4)
C(30)–C(25)	1.388(7)	C(6)–C(1)	1.393(6)	C(18)–C(13)	1.384(5)	C(29)–C(30)–C(25)	119.1(5)	C(5)–C(6)–C(1)	118.4(4)	C(17)–C(18)–C(13)	119.2(4)
C(31)–C(32)	1.386(6)	C(7)–C(8)	1.376(6)	C(19)–C(20)	1.391(5)	C(36)–C(31)–C(32)	119.8(4)	C(12)–C(7)–C(8)	120.5(4)	C(24)–C(19)–C(20)	121.0(4)
C(32)–C(33)	1.383(8)	C(8)–C(9)	1.386(6)	C(20)–C(21)	1.398(7)	C(31)–C(32)–C(33)	118.9(5)	C(7)–C(8)–C(9)	119.4(5)	C(19)–C(20)–C(21)	117.9(4)
C(33)–C(34)	1.364(9)	C(9)–C(10)	1.364(9)	C(21)–C(22)	1.365(8)	C(32)–C(33)–C(34)	121.5(5)	C(8)–C(9)–C(10)	120.3(5)	C(20)–C(21)–C(22)	121.2(5)
C(34)–C(35)	1.377(8)	C(10)–C(11)	1.370(10)	C(22)–C(23)	1.376(7)	C(33)–C(34)–C(35)	119.1(5)	C(9)–C(10)–C(11)	120.2(5)	C(21)–C(22)–C(23)	120.5(5)
C(35)–C(36)	1.380(8)	C(11)–C(12)	1.383(7)	C(23)–C(24)	1.387(7)	C(34)–C(35)–C(36)	120.3(6)	C(10)–C(11)–C(12)	120.4(6)	C(22)–C(23)–C(24)	119.8(4)
C(36)–C(31)	1.374(8)	C(12)–C(7)	1.382(7)	C(24)–C(19)	1.386(6)	C(35)–C(36)–C(31)	120.3(7)	C(11)–C(12)–C(7)	119.2(5)	C(23)–C(24)–C(19)	119.6(4)

TABLE 3 (*continued*)

(*b*) For (2)

Te(1)–O(14)	1.986(3)	Te(2)–O(24)	2.015(3)	O(14)–Te(1)–O(11)	163.6(1)	O(24)–Te(2)–O(21)	160.6(2)
Te(1)–O(11)	2.449(4)	Te(2)–O(21)	2.282(4)	O(14)–Te(1)–O(24)	88.8(1)	O(24)–Te(2)–O(14)	85.0(1)
Te(1)–O(24)	1.887(3)	Te(2)–O(14)	1.912(4)	O(14)–Te(1)–C(11)	89.2(2)	O(24)–Te(2)–C(21)	88.0(2)
Te(1)–C(11)	2.091(6)	Te(2)–C(21)	2.094(6)	O(11)–Te(1)–O(24)	76.1(1)	O(21)–Te(2)–O(14)	76.9(1)
Te(1) · · · O(21)	3.057(4)	Te(2) · · · O(23)	2.862(5)	O(11)–Te(1)–C(11)	85.4(2)	O(21)–Te(2)–C(21)	84.5(2)
Te(1) · · · O(12)	3.175(5)	Te(2) · · · O(21′)	3.405(4)	O(24)–Te(1)–C(11)	93.5(2)	O(14)–Te(2)–C(21)	94.9(2)
Te(1) · · · O(11′)	3.332(4)	Te(2) · · · O(13″)	3.514(6)				
Te(1) · · · O(13′)	3.453(5)	Te(2) · · · O(12‴)	3.409(5)				
Te(1) · · · O(12″)	3.277(5)						
Te(1) · · · O(13″)	3.479(6)						
				O(11)–N(11)–O(12)	119.2(5)	O(21)–N(21)–O(22)	118.2(6)
				O(11)–N(11)–O(13)	116.9(5)	O(21)–N(21)–O(23)	116.4(5)
				O(12)–N(11)–O(13)	123.8(5)	O(22)–N(21)–O(23)	125.3(6)
				Te(1)–O(11)–N(11)	115.9(3)	Te(2)–O(21)–N(21)	109.9(3)
				Te(1)–C(11)–C(12)	119.5(5)	Te(2)–C(21)–C(22)	120.6(10)
				Te(1)–C(11)–C(16)	119.3(4)	Te(2)–C(21)–C(26)	120.6(8)
N(11)–O(11)	1.294(6)	N(21)–O(21)	1.314(7)			Te(2)–C(21)–C(221)	116.6(9)
N(11)–O(12)	1.219(7)	N(21)–O(22)	1.205(8)			Te(2)–C(21)–C(261)	119.8(8)
N(11)–O(13)	1.225(7)	N(21)–O(23)	1.231(8)	Te(1)–O(14)–Te(2)	121.4(2)	Te(2)–O(24)–Te(1)	124.0(2)
C(11)–C(12)	1.383(7)	C(21)–C(22)	1.33(3)	C(16)–C(11)–C(12)	121.2(6)	C(26)–C(21)–C(22)	118(1)
C(12)–C(13)	1.391(10)	C(22)–C(23)	1.41(3)	C(11)–C(12)–C(13)	118.9(7)	C(21)–C(22)–C(23)	120(2)
C(13)–C(14)	1.368(12)	C(23)–C(24)	1.26(3)	C(12)–C(13)–C(14)	120.5(6)	C(22)–C(23)–C(24)	121(2)
C(14)–C(15)	1.398(8)	C(24)–C(25)	1.38(3)	C(13)–C(14)–C(15)	120.2(7)	C(23)–C(24)–C(25)	123(1)
C(15)–C(16)	1.384(11)	C(25)–C(26)	1.41(2)	C(14)–C(15)–C(16)	119.4(7)	C(24)–C(25)–C(26)	117(2)
C(16)–C(11)	1.373(10)	C(26)–C(21)	1.39(2)	C(15)–C(16)–C(11)	119.8(5)	C(25)–C(26)–C(21)	120(2)
		C(21)–C(221)	1.39(2)			C(261)–C(21)–C(221)	124(2)
		C(221)–C(231)	1.40(3)			C(21)–C(221)–C(231)	115(2)
		C(231)–C(24)	1.37(3)			C(221)–C(231)–C(24)	122(2)
		C(24)–C(251)	1.35(3)			C(231)–C(24)–C(251)	117(1)
		C(251)–C(261)	1.39(3)			C(24)–C(251)–C(261)	122(2)
		C(261)–C(21)	1.32(3)			C(251)–C(261)–C(21)	119(2)

(*c*) For (3)

Te–O(1)	2.171(3)	O(1)–Te–O(1′)	164.8(1)
Te–C(1)	2.108(5)	O(1)–Te–C(1)	88.8(2)
		O(1′)–Te–C(1)	81.5(2)
Te · · · O(3)	2.904(5)		
Te · · · O(2′)	3.205(5)	C(1)–Te–C(1′)	100.7(2)
N(1)–O(1)	1.328(6)	O(1)–N(1)–O(2)	116.3(5)
N(1)–O(2)	1.211(6)	O(1)–N(1)–O(3)	118.0(5)
N(1)–O(3)	1.217(6)	O(2)–N(1)–O(3)	125.7(5)
		Te–O(1)–N(1)	112.2(3)
		Te–C(1)–C(2)	119.9(4)
		Te–C(1)–C(6)	118.1(4)
C(1)–C(2)	1.379(8)	C(6)–C(1)–C(2)	121.8(5)
C(2)–C(3)	1.379(8)	C(1)–C(2)–C(3)	118.4(5)
C(3)–C(4)	1.379(9)	C(2)–C(3)–C(4)	120.5(6)
C(4)–C(5)	1.371(10)	C(3)–C(4)–C(5)	120.6(6)
C(5)–C(6)	1.392(9)	C(4)–C(5)–C(6)	119.7(6)
C(6)–C(1)	1.377(7)	C(5)–C(6)–C(1)	118.8(6)

and slow evaporation gave colourless needles of (2). Compound (3) was prepared by dissolving compound (1) in hot water–concentrated HNO_3 (1 : 9) and allowing the solution to cool slowly. Repeated heating and cooling eventually gave well formed crystals. The crystals of (3) deteriorate when exposed to moist air and are thought to be hydrolysed to the basic nitrate (1). Compound (3) was stored under 90% aqueous HNO_3. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 580B spectrophotometer.

Crystallographic Study.—The following procedure was adopted to minimise decomposition of (3). A few crystals in nitric acid were placed on a microscope slide. A suitably sized well formed crystal was mounted by touching it with a quartz fibre greased at one end with Apiezon. The mounted crystal moist with nitric acid was then sealed in a Lindemann tube and quickly cooled to 233 K with the Syntex LT-1 attachment to prevent decomposition and to harden the Apiezon grease. Complexes (1) and (2) were mounted conventionally. Crystal data are presented in Table 1; Mo-K_α radiation (λ = 0.710 69 Å) was used throughout.

Unit-cell constants were determined by least-squares fits to the positions of 15 reflections using the standard programs of a Syntex $P2_10$—50 four-circle diffractometer. Data were collected in the range 2θ = 0—50° with variable scan rates of 3—29° min^{-1} depending on the intensity of a 2-s prescan; the total background time was half the scan time. The intensities of three standard reflections were measured every 300 reflections and for (1) and (2) showed no significant change during data collection; (3) showed a slight regular decrease in the intensity during data collection for which a correction was made. Lorentz, polarisation, and absorption corrections were applied (the last with ABSCOR [4]). Refinement was carried out on the observed reflections [$I/\sigma(I) \geqslant 3.0$]. The positions of the tellurium atoms in (1)—(3) were located from Patterson functions. The remaining non-hydrogen atoms were located by difference-Fourier synthesis and anisotropic least-squares refinement using the X-RAY 76 programs.[5] For (1), phenyl hydrogen atoms were input in calculated positions with fixed isotropic thermal parameters and not refined; the proton attached to O(11) was not located and was omitted in the final refinement. Difference-Fourier synthesis for (3) revealed all the hydrogen atoms which were refined isotropically, while for (2) it revealed the protons attached to C(12)—C(16) but disordering of atoms C(21)—(26). The disordered atoms were refined with half occupancy including H atoms in calculated positions, with fixed thermal parameters.

For all three compounds empirical weighting schemes were used giving reduced weight to reflections with high and low F and $(\sin\theta)/\lambda$. Final R values were 0.022, 0.026, and 0.031 for (1), (2), and (3) respectively. Scattering factors were taken from ref. 6 in the analytical form; computing was carried out on a Burroughs B6700 for (2) and (3) at Warwick University and on a CDC7600 at Manchester University for (1). Table 2 contains atomic co-ordinates and Table 3 bond lengths and angles. Structure factors and thermal parameters are listed in Supplementary Publication No. SUP 23280 (56 pp.).*

RESULTS AND DISCUSSION

The preparations of several aryltellurium nitrates have been reported in the literature.[7-9] Diaryl tellurides are converted into dinitrates by treatment with *ca*. 5 mol dm^{-3} nitric acid, but are recovered as the anhydrides, $[R_2Te(NO_3)]_2O$ (R = aryl).[7] Telluroxides dissolve in concentrated nitric acid to give dinitrates.[8] Diaryl tellurides are also reported to form hydroxynitrates, $R_2Te(NO_3)(OH)$,[8] with dilute nitric acid and hot nitric acid is reported to oxidise diphenyl ditelluride to the benzenetellurinic acid nitrate ester, $PhTeONO_3$.[9]

We have prepared the three aryltellurium nitrates (1), (2), and (3) in order to clarify the chemistry of these compounds and investigate the nature of the bonding. We have been unable to prepare $[Ph_2Te(NO_3)]_2O$ or $Ph_2Te(NO_3)(OH)$ as described, but we have obtained by two methods a basic nitrate (1) that is a 1 : 1 combination of these two nitrates. Compounds (2) and (3) correspond to those described in the literature.[8,9]

The i.r. spectra of the three compounds are complex due to the many vibrations of the phenyl rings and assignment of the peaks is difficult. The peaks in the region 250—800 cm^{-1} [400—800 cm^{-1} for (3)] and tentative assignments are presented in Table 4. In (1), peaks at 607 and 426 cm^{-1} may be attributed to $\nu_{asym.}$ and ν_{sym} of the Te–O–Te bridge by comparison with μ-oxo-bis-[nitratophenyliodine(III)] [10,11] ($\nu_{asym.}$ 585, $\nu_{sym.}$ 427 cm^{-1} I–O–I). For (2), strong bands at 627 and 498 cm^{-1} may be assigned similarly. At lower frequencies both (1) and (2) exhibit absorption in the region 273—280 cm^{-1} which possibly arises from Te–O–Te. All three compounds exhibit bands due to nitrate groups and benzene rings in the region 800—4 000 cm^{-1}.

TABLE 4

Infrared absorption frequencies (cm^{-1}) in the range 250—800 cm^{-1} [400—800 cm^{-1} for (3)]

(1)	(2)	(3)	Assignment
	768s	789m	
746s	741 (sh)	743m	C_6H_5, out-of-plane C–H deformation
739s	736s	733s	
709w	721m	720m	$\nu_3\nu_5$ NO_3^-
	715w		
	705w	702m	
691s	685 (sh)	683m	C_6H_5, out-of-plane C–H deformation
673s	680m		
660 (sh)			
607m	627vs		Te–O–Te $\nu_{asym.}$
426 (sh)	498vs		Te–O–Te $\nu_{sym.}$
472m	458m	465m	Te–C stretch
462 (sh)	446m	450m	
	336m		
280m	273m		

The three structures are contrasting but in each case the Te atoms adopt four-fold primary co-ordination with distorted trigonal-bipyramidal geometry with axial nitrate groups, equatorial lone pairs, and several secondary interactions clustered around the lone pair. Compounds (1) and (2) also contain μ-oxo-bridging.

Compound (1) (Figure 1) is the most complex structure and contains three Te atoms in the asymmetric unit. Each Te atom is four-co-ordinate with two equatorial phenyl groups (mean Te–C 2.11 Å), one short axial Te–O bond (mean 1.98 Å) [to terminal OH for Te(1), and in symmetrical μ-oxo-bridges for Te(2) and Te(3)], and one

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

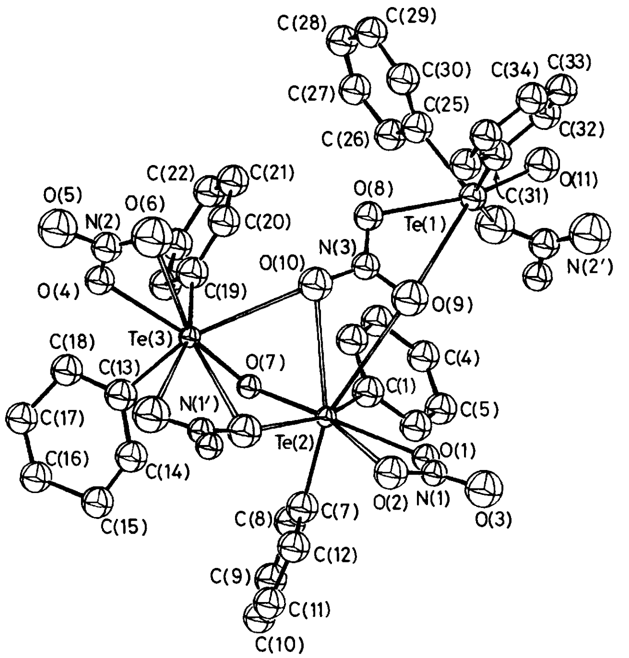


FIGURE 1 Molecular structure of (1), showing atomic numbering. The long Te · · · O interactions are shown as outline bonds

longer axial Te–O bond (mean 2.48 Å) to a nitrate group. The overall geometry is that of a distorted trigonal bipyramid with the vacant equatorial position occupied by the lone pair (mean $C_{eq.}$–Te–$C_{eq.}$ 98.6°; mean $O_{ax.}$–Te–$O_{ax.}$ 166.8°). The whole asymmetric unit is loosely held together by several secondary bonds (Figure 1) from nitrate oxygens to Te atoms (Te–ONO_2 2.940—3.415 Å). The secondary bonds do not show regular geometries at the Te atoms, unlike Ph_2TeCl_2 or Ph_2TeO,[12] but are grouped around the lone pair; some arise from quasi-bidentate nitrate groups. The only link between different complex units occurs along *a*, through the weak Te(1) · · · O(5) contact.

Compound (2) (Figure 2) adopts a polymeric structure with two oxygen-bridged Te atoms in the asymmetric unit, further bridged by oxygen to adjacent asymmetric units to give polymeric chains running parallel to *b* (Figure 3). Interactions between phenyl rings related by the short *b*-axis translation may also be important in the packing. The μ-oxo-bridging is nearly symmetrical,

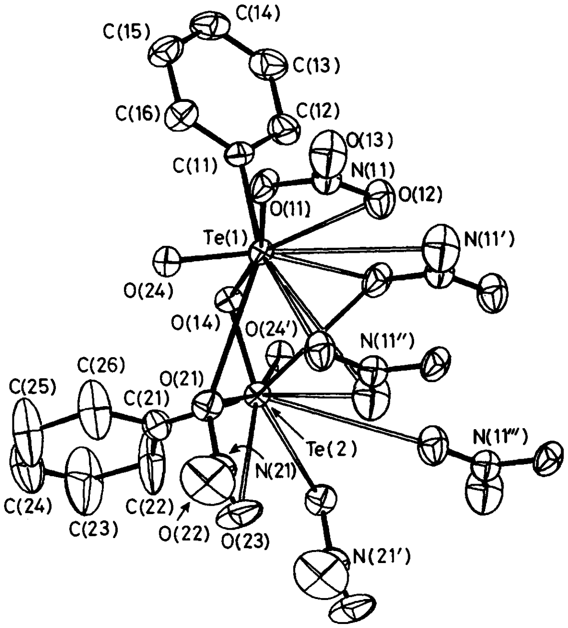


FIGURE 2 Molecular structure of (2), showing atomic numbering

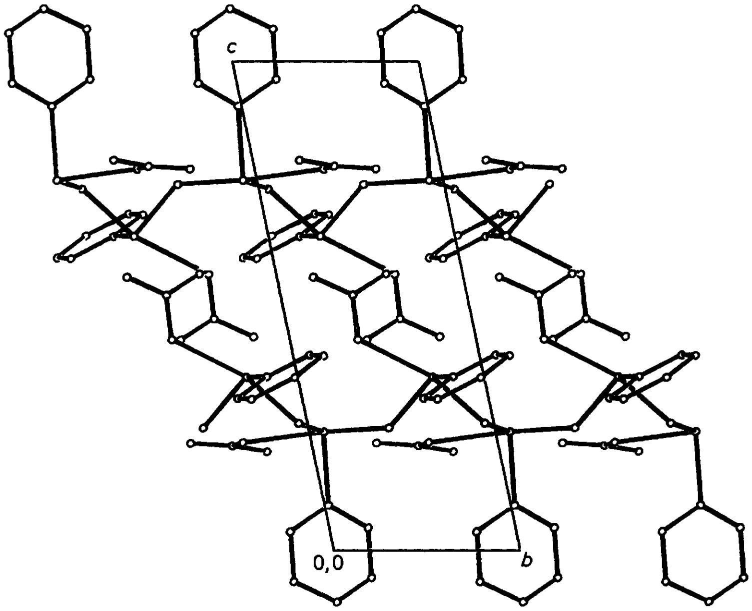


FIGURE 3 Packing diagram for (2), viewed down *a*

Te–O varying from 1.887(3) to 2.015(3) Å. Each Te has one phenyl carbon atom attached to it, and a nitrate oxygen completes its primary geometry. The Te–O (bridge) bonds are, as in (1), significantly shorter than the Te–ONO_2 bonds (mean 2.37 Å). The co-ordination is again trigonal bipyramidal at Te but somewhat more distorted than in (1) (mean $O_{eq.}$–Te–$C_{eq.}$ 94.18°; mean $O_{ax.}$–Te–$O_{ax.}$ 163.08°). The parallel chains are loosely held together by many weak secondary interactions (<3.5 Å) which, as in (1), cluster around the vacant co-ordination site and do not complete a regular geometry (Figure 2).

The structure of (3) is simpler (Figure 4). The Te atom lies in special position 4*e* in space group *C*2/*c*. Each Te atom is bonded to two symmetry-related phenyl rings and two symmetry-related nitrate groups. The nitrate ions are asymmetrically bidentate with a primary Te–ONO_2 bond [Te–O(1) 2.171(3) Å] and a secondary interaction [Te · · · O(3) 2.904(5) Å].

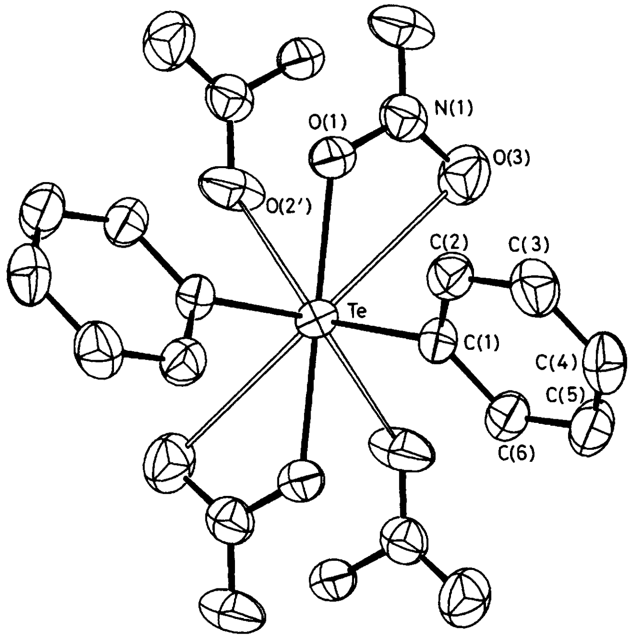


FIGURE 4 Molecular structure of (3), showing atomic numbering

Each nitrate ion further participates in another secondary bond, Te · · · O(2′) 3.205(5) Å. The four primary bonds at each Te again have trigonal-bipyramidal geometry with equatorial phenyl rings and a cluster of four secondary bonds oriented around the lone pair in the vacant equatorial site. The secondary Te · · · ONO_2 interactions link neighbouring molecules into chains parallel to *c* (Figure 5). The primary Te–ONO_2 bond in (3) is shorter than any Te–ONO_2 bonds found in (1) and (2) [mean Te–ONO_2 2.48 Å in (1) and 2.36 Å in (2)] which would suggest a more covalent tellurium–nitrate interaction.

In all three compounds the nitrate ions are distorted from C_{3v} symmetry. The distortions are greater for (2) and (3) which both show increases in one O–NO_2 bond (for the oxygen linked to Te) to *ca.* 1.30 Å and an opening out of the opposite $\mathrm{N}{<}^{\mathrm{O}}_{\mathrm{O}}$ angle to *ca.* 125°. In (1), the O–NO_2 distances are around 1.27 Å with $\mathrm{N}{<}^{\mathrm{O}}_{\mathrm{O}}$ angles around 122°. This suggests that in (1) the nitrate is more ionically bound than in (2) or (3).

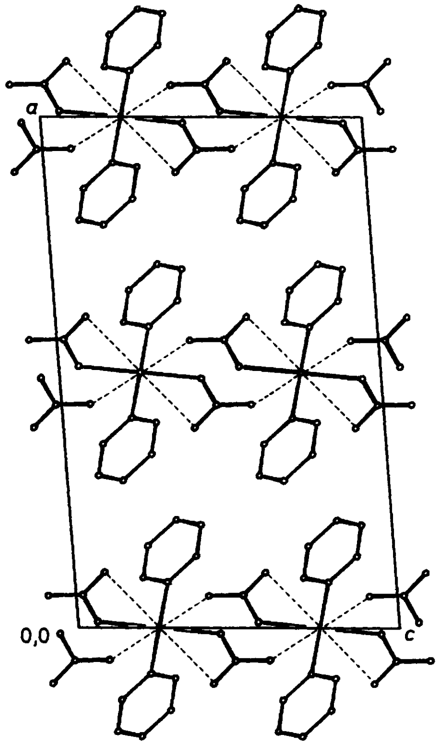
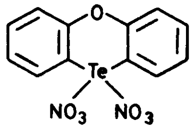
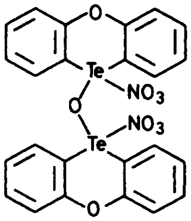


FIGURE 5 Packing diagram for (3), viewed down *b*

The most directly comparable structures are those of two phenoxatellurin nitrates.[13] These are respectively a dinitrate (I) and an oxo-bridged dimer (II) of which the former is apparently more stable; this is surprising in view of the much greater stability of the μ-oxo-species (1), compared to (3). Both the phenoxatellurin compounds have very similar primary geometry around Te to (1) and (3), and again both form a series of longer Te · · · O contacts around the lone pair, including contacts to a second atom of each nitrate group. Distinctive features are the transannular Te · · · O contacts of *ca.* 3.3 Å;



(I)



(II)

however, these are probably not of chemical significance, but are consequences of the nature of the structures.

All the structures (1)—(3) contrast with those of the basic iodine nitrate[3] discussed earlier and with diphenyliodonium nitrate.[14] The two lone pairs on the central atom in the iodine(III) compounds produce a planar geometry around the iodine atoms. In diphenyliodonium nitrate the geometry is square planar with bridging nitrate ions giving rise to infinite zigzag chains. In the basic iodine nitrate the primary geometry about the iodine is T shaped but two secondary bonds from nitrate oxygens give rise to a pentagonal planar geometry and hold the molecules into loose chains. In the latter the I–O–I angle of 123.7(6)° is comparable to the Te–O–Te angles observed in (1), 125.5(1)°, and (2), 121.4(2) and 124.0(2)°, indicative of π interaction between the p orbitals of these bridging oxygens and the d orbitals of the tellurium or iodine. The contrasting pattern of secondary interactions for Te is seen most clearly in (3) with its four Te $\cdots$ O contacts placed around the lone pair and staggered with respect to the primary bonds. Similar arrangements are found in (1) and (2), although the greater complexity of the molecules themselves is probably responsible for the more complex patterns of interactions, including the formation of only two links to Te(1) in (1), and of five and six links in (2).

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