THE OXIDES AND OXYACIDS OF TELLURIUM

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A critical review of the oxides and oxyacids of tellurium is presented. The crystal chemistry of the compounds is discussed in detail. The average bond distances and angles of the $Te(IV)O_4$, $Te(VI)O_6$, Te(VI)–O–H...O–Te(VI) and Te–O–Te groups have been calculated by statistical evaluation of the geometry of the structures. The deviations of $Te(VI)O_6$ from the average geometry were quantitatively characterized by distortion indices. The $Te(IV)O_4$ and $Te(VI)O_6$ groups were evaluated also by

the bond valences s(Te–O). The compounds whose distortion indices or Σs(Te–O) values were outside the interval $\bar{x} \pm 3\sigma$ should be checked.

1. INTRODUCTION

This paper presents a critical review of the crystal chemistry, preparation and some properties of the oxides and oxyacids of tellurium. Earlier similar reviews were published by Dutton and Cooper[1], Bayer[2] and Lindqvist[3].

All oxides and oxyacids belonging to the TeO_2–TeO_3–H_2O system are plotted in a schematic phase diagram, see Fig. 1.

In all the compounds with Te(IV) discussed here, the Te atoms are present in a distorted trigonal bipyramidal enviroment in which they are bonded to four oxygen atoms and a stereochemically active lone-pair is assumed to occupy the fifth coordinate position in the equatorial plane[4]. Distances Te(IV)–O(a, b, c, d) are denoted as a, b, c, d, angles O(a)–Te(IV)–O(b) as a–b etc., see Fig. 2. The criteria for labelling are: a–b → 180°, a ≤ b, c ≤ d.

In Te(VI) compounds, the Te atoms are octahedrally coordinated with oxygen atoms in the form of a distorted octahedron. Distances Te(VI)–O(A, B, C, D, E, F) are denoted as A, B, C, D, E, F, angles O(A)–Te(VI)–O(B) as A–B etc., see Fig. 3. The criteria for labelling are: A ≤ B, C, D, E, F, A–B → 180°, C ≤ D, E, F, C–D → 180°, E ≤ F.

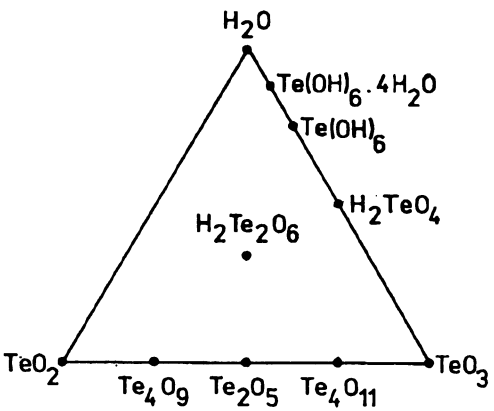

FIG. 1
Oxides and oxyacids in the TeO_2–TeO_3–H_2O system

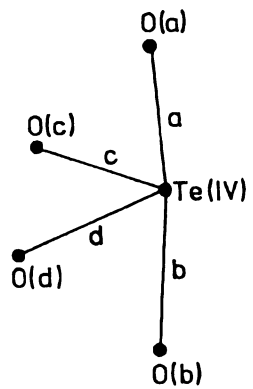

FIG. 2
Schematic representation and labelling of the atoms in the Te(IV)–O_4 formation (denotation see text)

The primary data for the calculations of the distances and angles were the published lattice parameters and the atomic coordinates. All the distances and angles were recalculated and the most important data* are given in Table I.

The 53 compounds studied contain 6 $Te(IV)O_4$ and 53 $Te(VI)O_6$ formations. Figure 4 depicts histogram for the Te(VI)–O distances (n = 354), Fig. 5 depicts histogram for the O–Te(VI)–O angles → 180° (n = 177) and Fig. 6 depicts histogram for the O–Te(VI)–O angles → 90° (n = 708).

The symmetries of the $Te(IV)O_4$ and $Te(VI)O_6$ formations are given in Table II.

2. TELLURIUM DIOXIDES TeO_2

Tellurium oxide can be prepared by a number of methods, the most important being the thermal decomposition of hexaoxotelluric acid[5] and the action of concentrated nitric acid on metallic tellurium with the contingent thermal decomposition of the basic tellurium nitrate formed[6]. The oxide solubility is very poor in water, higher in aqueous sodium hydroxide solution and good in concentrated hydrochloric acid.

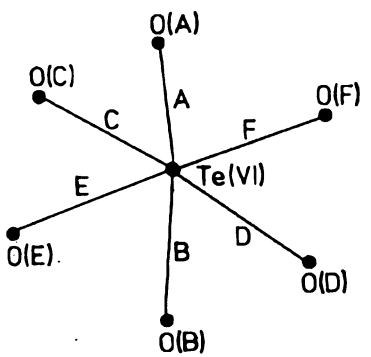

FIG. 3
Schematic representation and labelling of the atoms in the Te(VI)–O_6 formation (denotation see text)

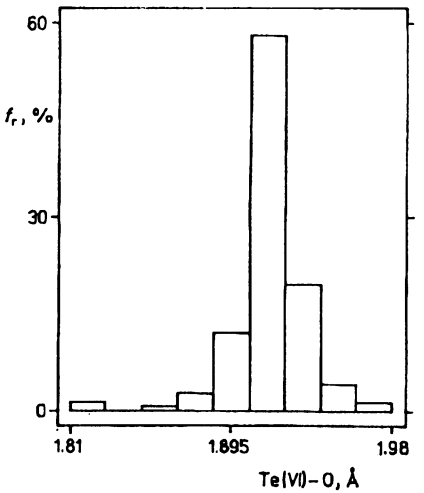

FIG. 4
A histogram of the Te(VI)–O distances (f_r is the relative frequency). The class width is 0.01889 Å, n = 354

* Lists of the complete data can be obtained through the author.

TABLE I
Te–O distances (Å) and O–Te–O angles (deg) in $Te(IV)O_4$ and $Te(VI)O_6$ formations[a]

No. of compound	Compound	Modification Note	a a–b	b c–d	c a–c	d b–d	A A–B	B C–D	C E–F	D A–C	E B–E	F D–F
I	TeO_2	α	2.1210(6)	2.1210(6)	1.8796(5)	1.8796(5)						
			167.94(4)	103.34(4)	88.34(1)	88.34(1)						
II	TeO_2	β	2.07(2)	2.20(2)	1.88(2)	1.93(2)						
			168(1)	101(1)	90(1)	90(1)						
III	TeO_2	γ	2.03(2)	2.11(2)	1.91(2)	2.04(2)						
			163(1)	102(1)	80(1)	82(1)						
IV	Te_4O_9		2.020(9)[6]	2.144(8)[4]	1.883(8)[4]	1.902(9)[6]	1.903(8)[4]	1.948(9)[4]	1.903(8)[4]	1.948(9)[4]	1.903(4)[4]	1.948(9)[4]
			172.0(3)	98.5(4)	90.8(3)	90.1(3)	176.4(3)	176.4(3)	176.4(3)	88.7(3)	94.6(4)	86.7(4)
V	Te_2O_5		2.072(5)[6]	2.080(6)[4]	1.892(6)[4]	1.913(4)[6]	1.848(4)[4]	1.929(4)[4]	1.907(5)[6]	1.972(4)[6]	1.927(5)[6]	1.933(4)[6]
			165.9(2)	91.0(2)	86.0(2)	81.8(2)	175.9(2)	173.5(2)	171.4(2)	97.5(2)	88.9(2)	91.5(1)
VI	Te_4O_{11}		probably identical with γ-TeO_3									
VII	TeO_3	α	amorphous									
VIII	TeO_3	β					1.91(1)	1.91(1)	1.91(1)	1.91(1)	1.91(1)	1.91(1)
							180	180	180	90.9(3)	89.1(3)	90.9(3)
IX	TeO_3	γ	atomic coordinates not determined									
Xa	$Te(OH)_6$	$Fd\bar{3}c$					1.912(6)	1.912(6)	1.912(6)	1.912(6)	1.912(6)	1.912(6)
							180	180	180	89.8(3)	89.8(3)	89.8(3)
Xb		$F4_132$					1.90(2)	1.94(2)	1.90(2)	1.94(2)	1.90(2)	1.94(2)
							178(2)	178(2)	178(2)	91(1)	89(1)	89(1)
Xc		$F4_132$, *N*					1.81(1)	1.98(1)	1.81(1)	1.98(1)	1.81(1)	1.98(1)
							175.7(4)	175.7(4)	175.7(4)	87.5(3)	88.3(3)	90.6(3)

TABLE I
(*Continued*)

No. of compound	Compound	Modification Note	a a–b	b c–d	c a–c	d b–d	A A–B	B C–D	C E–F	D A–C	E B–E	F D–F
XIa	$Te(OH)_6$	*m*					1.905(5)	1.905(5)	1.915(5)	1.915(5)	1.918(5)	1.918(5)
							180	180	180	92.2(2)	88.4(2)	89.1(2)
							1.912(5)	1.912(5)	1.918(4)	1.918(4)	1.929(5)	1.929(5)
							180	180	180	87.8(2)	91.1(2)	91.5(2)
XIb		*N*					1.907(1)	1.907(1)	1.908(1)	1.908(1)	1.910(1)	1.910(1)
							180	180	180	91.29(7)	91.04(6)	92.09(7)
							1.908(1)	1.908(1)	1.909(1)	1.909(1)	1.914(1)	1.914(1)
							180	180	180	87.65(6)	90.64(7)	91.60(6)
XII	$Te(OH)_6$	*t*	atomic coordinates not determined									
XIII	$Te(OH)_6 . 4 H_2O$		atomic coordinates not determined									
XIV	H_2TeO_4						$1.903(8)^H$	$1.903(8)^H$	$1.906(8)^6$	$1.906(8)^6$	$1.930(8)^6$	$1.930(8)^6$
							180	180	180	88.6(4)	86.3(4)	91.0(2)
XV	$H_2Te_2O_6$		$2.063(5)^6$	$2.106(5)^4$	$1.862(6)^4$	$1.937(4)^6$	$1.865(5)^4$	$1.909(4)^4$	$1.904(5)^H$	$1.951(5)^6$	$1.937(5)^H$	$1.939(5)^6$
			171.8(2)	91.0(2)	88.9(2)	84.1(2)	178.1(2)	174.4(2)	172.8(2)	93.5(2)	87.0(2)	92.0(2)
I – XV	mean values,											
	n^*(TeIV)=6		2.06(4)	2.13(4)	1.88(2)	1.93(6)	1.89(3)	1.92(2)	1.90(3)	1.93(3)	1.91(3)	1.93(3)
	n^*(TeVI)=12		168(3)	98(5)	87(4)	86(4)	179(2)	178(2)	178(3)	91(3)	90(2)	90(2)
XVI – LIII	$Te(OH)_6$. adducts,											
	n^* = 47						1.90(2)	1.91(2)	1.91(1)	1.92(1)	1.92(1)	1.92(1)
							178(3)	179(2)	178(3)	91(2)	90(3)	90(2)
IV – LIII									1.915(20)	(n = 354)		
							178.4(2.6)	(n = 177)		90.0(2.3)	(n = 708)	

[a] For the significance of symbols a....d a A....F see the text. Indices 4, 6, H denote oxygen atoms further bound to Te(IV), Te(VI) or H. *N* denotes the values determined by neutron data. The values in parentheses are e.s.d.'s or e.s.d.'s of the arithmetic means and n is the number of values used in calculation. n^* is the number of compounds.

Two standard modifications of tellurium dioxide were found: synthetic paratellurite α-TeO_2 and mineral tellurite β-TeO_2. Complications in polymorphism of TeO_2 appear in studies conducted at higher pressures and temperatures[7,8].

2.1. *Paratellurite α-TeO2 (I)*

The earliest attempt at a determination of the paratellurite structure was made by Goldschmidt[9], who reported a structure of the rutile type (space group *P4/mmm*). Stehlík and Balák[10] redetermined the structure from single crystal X-ray data and found

TABLE II
Symmetries of Te(IV)O_4 (n = 6) and te(VI)O_6 (n = 53) formations

Symmetry	Te(IV)O_4	Te(VI)O_6
Highest possible symmetry	*mm*2	$m\bar{3}m$
Number of sub-groups	3	24
Point groups found	1 2	1 $\bar{1}$ 2 3 $\bar{3}$ 32
Number of formations in the point groups	5 1	14 26 1 5 6 1

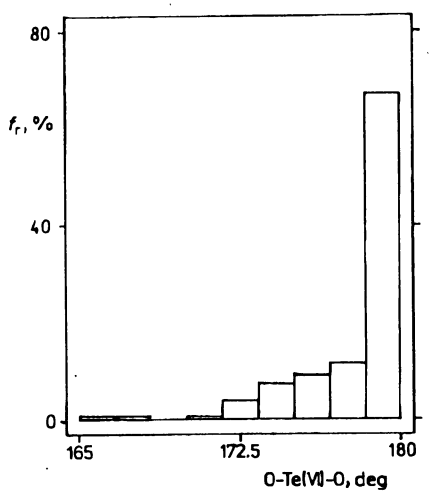

FIG. 5
A histogram of the O–Te(VI)–O angles → 180° (f_r is the relative frequency). The class width is 1.6667°, n = 177

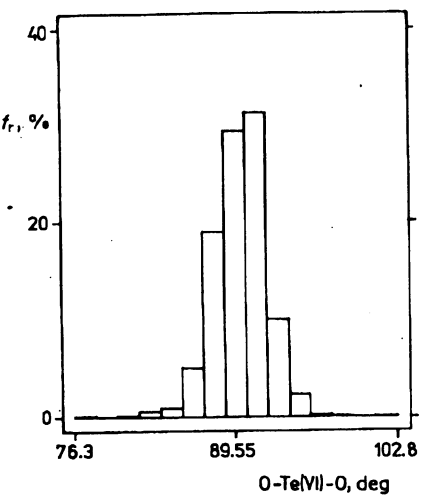

FIG. 6
A histogram of the O–Te(VI)–O angles → 90° (f_r is the relative frequency). The class width is 1.7667°, n = 708

the space groups $P4_12_12$ or $P4_32_12$. Leciejewicz[11] investigated the structure by neutron powder diffraction and confirmed the assignement of one of the latter space groups. The structural parameters have been refined using three-dimensional X-ray dat[12]. Paratellurite belongs to space group $P4_32_12$, a = 4.810(1), c = 7.613(2) Å (ref.[13]) or $P4_12_12$ (ref.[14]). The intramolecular distances and angles are given in Table I. Each oxygen atom is bonded to two tellurium atoms, so that the –O–Te–O–Te– bonds form a three-dimensional network. The stoichiometry can be described by the formula $[Te(O_{0.5})_4]_{3\infty}$. Density D_x equals 6.017(1) Mg m^{-3} and Z = 4. The Czochralski method resulted in large prefect crystals, up to 60 mm in length and 25 mm in diameter[6]. This material is of interest in piezoelectric and electrooptic applications. Paratellurite is also found in Mexico as a mineral[15]. The bands of infrared spectrum in the 500 – 850 cm^{-1} region were assigned in the following manner: 780 A_1, ν^s_{eq}, 714 B_1, ν^{as}_{eq}, 675 B_2, ν^{as}_{ax} and 635 cm^{-1} A_1, ν^s_{ax} (ref.[16]). The Raman spectra in the regions 40 – 160 and 10 – 700 cm^{-1} were published in refs[17,18]. A far-infrared spectrum has also been published in ref.[18]. The isomer shift and quadrupole splitting in the ^{125}Te Mössbauer spectra can be explained by ca 9% *s*-character in the bonding orbitals. The tellurium atoms would then have an approximate electronic configuration $5s^{1.6}$ $5p^{1.9}$, i.e. the effective charge on the tellurium atoms would be ca +2.5 (ref.[19]).

2.2. *Tellurite β-TeO$_2$ (II)*

Oxide β-TeO_2 was found as a mineral. It was originally ascribed the structure of distorted brookite[20]. The correct structure was found by Beyer et al.[21] and refined by Beyer[22] to space group *Pbca* with a = 12.035(6), b = 5.464(3), c = 5.607(3) Å. The intramolecular distances and angles are given in Table I. Pairs of TeO_4 groups are connected to form Te_2O_6 units and these are further linked to form sheets. The stoichiometry can be described by the formula $[Te(O_{0.5})_4]_{2\infty}$. Density D_x equals 5.748(1) Mg m^{-3} and Z = 8. The similarities between the Mössbauer spectra of the two modifications indicate that there is no significant difference between them in the electronic structure and the chemical bonding[23].

2.3. *Very High Pressure Modifications of TeO$_2$*

TeO_2 is dimorphous at the atmospheric pressure. According to Switzer and Swanson[15], tellurite transforms into paratellurite at 873 K. The high temperature paratellurite must also be considered as a high pressure modification, in view of its higher density. It is surprising that paratellurite is not converted into tellurite on cooling[6].

The next phase transition is the well studied second-order transition from $P4_32_12$ ($P4_12_12$) symmetry to $P2_12_12_1$ symmetry. This modification is denoted as γ-TeO_2 (*III*). The structure parameters of γ-TeO_2 have been obtained by time-of-flight neutron diffraction at 1.98 GPa and 296 K (a = 4.6053(6), b = 4.8557(6), c = 7.5300(10) Å, Z = 4,

ref.[24]). The intramolecular distances and angles are given in Table I. The oxygen and tellurium atoms connect with one another to form a three-dimensional network that can be described by the formula $[Te(O_{0.5})_4]_{3\infty}$. The dependence of the unit cell volume V, the volume of the formula species V_{fs} and the calculated density D_x on pressure P is given in Table III. The effect of the pressure on the Raman modes in α-TeO_2 paratellurite has been investigated up to 30 GPa, indicating four phase transitions near 1, 4.5, 11 and 22 GPa. The similarity in the Raman spectra of phases 1 to 4 suggest that only subtle changes in the structures are involved in these phase transitions. The totally different spectrum of phase 5 indicates major structural changes at 22 GPa by a first-order transition. It is suggested that the structure of this phase is similar to the $PbCl_2$ type[8].

2.4. *Amorphous TeO_2*

Crystalline TeO_2 melts at 1 003 K to yield an amorphous TeO_2 glass[25]. The Raman spectra of the tellurium dioxide glass obtained at 90 and 300 K were interpreted using a model consisting of a TeO_4 pyramid with *mm*2 symmetry[26].

3. OXIDE Te_4O_9 (*IV*)

This oxide can be prepared by hydrothermal synthesis starting with $Te(OH)_6$, TeO_2 and H_2O at 623 K. The structure has a hexagonal cell in space group $R\bar{3}$ with a = 9.320 and c = 14.485 Å (ref.[27]). The intramolecular distances and angles are given in Table I. The oxygen coordination of Te(IV) conforms to the usual description as a deformed trigonal

TABLE III
The dependence of the unit cell volume V (Å^3), of the formula species volume V_{fs} (Å^3), and of calculated density D_x (Mg m^{-3}) for TeO_2 on pressure P (GPa)

P	V	V_{fs}	D_x	Modification	References
0	184.3[a]	46.1	5.75	β	22
0	176.1	44.0	6.02	α	13
0.69	173.3	43.3	6.12	α	24
0.98	172.3	43.1	6.15	γ	24
1.98	168.4	42.1	6.29	γ	24
3.25	166.5	41.6	6.36	γ	24
8.5	155.0	38.7	6.84		7
11.0	150.3	37.6	7.05		7
24.9	135.6	33.9	7.82		7

[a] $V/2$.

bipyramid while the oxygen coordination of Te(VI) has been found to be octahedral. All the oxygen atoms from the $Te(VI)O_6$ octahedra are bonded with Te(IV) so that the $Te(VI)O_6$ and $Te(IV)O_4$ units build the layers. The stoichiometry can be described by the formula $\{[Te(VI)(O^4)_6] \cdot 6\ [Te(IV)(O^4)_2(O^6)_2\}_{3\infty}$. The superscripts ^{4} and ^{6} have the following significance: $Te(VI)(O^4)_6$ denotes that 6 oxygen atoms are bonded to the Te(VI) atoms and they are further bonded to Te(IV); $Te(IV)(O^4)_2(O^6)_2$ means that two oxygen atoms bonded to Te(IV) are further bonded to Te(IV) and two oxygen atoms bonded to Te(IV) are further bonded to Te(VI). These results agree with the Mössbauer spectra[28]. Density D_x equals 5.981 Mg m^{-3} and $Z = 6$. This oxide has also been obtained by thermal decomposition of hexaoxotelluric acid $Te(OH)_6$ (ref.[29]).

4. OXIDE Te_2O_5 (*V*)

Oxide Te_2O_5 was first prepared through thermal decomposition of $Te(OH)_6$ in the form of a powder[30]. Single crystals have been obtained by a hydrothermal synthesis and the structure determined as space group $P2_1$ with $a = 5.368$, $b = 4.696$, $c = 7.955$ Å, $\beta = 104.82°$ (ref.[31]). The intramolecular distances and angles are given in Table I. The coordination polyhedra of Te(VI) and Te(IV) are very similar to those in Te_4O_9. The TeO_6 octahedra are connected at the corners to form infinite sheets between which TeO_4 chains run, forming a three-dimensional network. The stoichiometry can be described by the formula $\{[Te(VI)(O^6)_4(O^4)_2]\ [Te(IV)(O^4)_2(O^6)_2]\}_{3\infty}$. Density D_x equals 5.741(1) Mg m^{-3} and $Z = 2$. The Mössbauer spectra showed the presence of both Te(VI) and Te(IV) atoms as distinct structural units[28,32]. The growth of crystals of milimeter size by a hydrothermal method and the pyroelectric behaviour of Te_2O_5 was described in ref.[33]. The infrared spectrum in the region of 400 – 4 000 cm^{-1} was published in ref.[34] and the Raman spectrum in the region of 100 – 900 cm^{-1} in ref.[35].

5. OXIDE Te_4O_{11} (*VI*)

This oxide is assumed to be an intermediate in the thermal decomposition of $Te(OH)_6$ (ref.[36]) but its existence as a chemical individuum has not been demonstrated. It can probably be classified among the group of γ-TeO_3 oxides.

6. TELLURIUM TRIOXIDES TeO_3

There exist a number of compounds denoted as tellurium trioxide TeO_3, but only crystalline β-TeO_3 is a real trioxide. The other substances are phases containing Te(VI), Te(IV), O^{2-}, OH^- and possibly also H_2O, O_2^- and O_2 in various ratios.

6.1. *Oxide α-TeO_3 (VII)*

Products whose weight losses or analytically determined amounts of tellurium correspond to TeO_3 can be prepared by thermal decomposition of $Te(OH)_6$. The product is an orange yellow, amorphous powder with a variable density of about 5.1 Mg m^{-3} (ref.[37]). In addition to Te(VI) its also contain Te(IV), O^{2-}, OH^- and possibly also H_2O, O_2^- and O_2 (refs[34,38]). The Mössbauer spectra also suggest the presence of Te(VI) and Te(IV) (ref.[38]). It seems that it is impossible to prepare pure TeO_3 through thermal decomposition of $Te(OH)_6$ in air, in a vacuum or in an inert atmosphere.

6.2. *Oxide β-TeO_3 (VIII)*

The true TeO_3 was first prepared as a grey-beige powder by Patry[37] using hydrothermal decomposition of $Te(OH)_6$. The structure was determined by Dumora and Hagenmuller[39] and refined by Dušek and Loub[40]. β-TeO_3 belongs to the space group $R\bar{3}c$, a = 4.901(2), c = 13.030(4) Å. The intramolecular distances and angles are given in Table I. The structure consists of nearly regular octahedra TeO_6, where each oxygen atom is bonded to two tellurium atoms so that the $[Te(VI)(O_{0.5})_6]_{3\infty}$ three dimensional network is formed. Density D_x equals 6.454(1) Mg m^{-3} and Z = 6. The infrared and Raman spectra of β-TeO_3 differ significantly from those of α-TeO_3: they are simpler and the lines sharper, with very strong lines at 336 (Ra) and 796 (IR) cm^{-1} (refs[38, 41]). The Mössbauer centre shift δ for β-TeO_3 has the same value as that for $Te(OH)_6$ (ref.[38]). It appears that it is impossible to prepare β-TeO_3 by hydrothermal synthesis as a powder or single crystal, but it is possible to prepare β-TeO_3 by heating α-TeO_3 with water in a glass sealed tube at 623 – 673 K. β-TeO_3 is insoluble in water, in concentrated hydrochloric acid and in concentrated aqueous potassium hydroxide solution[42]. In the preparation of β-TeO_3, the recommended addition of sulfuric acid[1,39] should be disregarded since $Te_2O_3SO_4$ may form[43].

6.3. *Oxide γ-TeO_3 (IX)*

Meyer discovered that the "TeO_3" oxide is paramagnetic as early as 1899 (ref.[44]). It was later confirmed that the products of the thermal decomposition of $Te(OH)_6$ in air or in a vacuum, with an approximate composition of TeO_3, were paramagnetic. These products are crystalline[34,45] (in ref.[45] the product denoted as TeO_3A) with the cell parameters a = 6.287, b = 4.938, c = 7.717 Å (ref.[36], the product denoted as α-TeO_3). The reaction of a concentrated aqueous solution of KOH in these products releases the oxygen, whose paramagnetic susceptibility corresponds to the susceptibility of the products. Therefore the paramagnetism was assigned to the presence of absorbed O_2 or the superoxide ion O_2^-. The electron spin resonance spectrum of the γ-TeO_3 products exhibits one very broad absorption band, which makes it impossible to exactly compute

the g-factor ($g \approx 2$, ref.[34]). Broad bands corresponding to the TeOH vibrations have been found in the infrared spectra[34,45]. Density D_{exp} decreases with the increasing paramagnetism of the products and the colour changes from yellowish to orange. These products contain Te(VI), Te(IV), O^{2-}, OH^-, O_2^- or O_2 (ref.[34]).]

7. HEXAOXOTELLURIC ACIDS $Te(OH)_6$

Hexaoxotelluric acid has been reported to exist in three crystalline modifications, cubic, monoclinic and tetragonal, although only one paper reported the tetragonal modification.

7.1. *$Te(OH)_6$ – Cubic Form (X)*

The structure of the $Te(OH)_6$ cubic form was first determined by Kirkpatrick and Pauling[46] with the space group $Fd\bar{3}c$. The structure has since been repeatedly studied. The X-ray structure refinement[47] confirmed the space group $Fd\bar{3}c$ with the cell parameter a = 15.705(3) Å. The intramolecular distances and angles are given in Table I (*Xa*). The structure is built up of discrete $Te(OH)_6$ octahedra. The intermolecular O...O distances indicate that each $Te(OH)_6$ entity participates in six relatively strong hydrogen bonds (2.63(1) Å) and six weaker bonds (2.77(1) Å). Density D_x equals 3.149(1) Mg m^{-3} and Z = 32. In contrast to the above diffraction conclusions, the neutron diffraction data require the assignment of the space group $F4_132$ with the cell parameter a = 15.699(2) Å (ref.[48]). The intramolecular distances and angles are given in Table I (*Xc*). The hydrogen atoms are statistically disordered into two equivalent positions. Twelve hydrogen bonds are associated with each telluric acid molecule. The X-ray structure determination in the space group $F4_132$ was published in the same paper[48]. The intramolecular distances and angles are given in Table I (*Xb*). Optimal conditions for preparation can be also found in the paper[49]. The infrared spectrum was studied in refs[38,48,49].

7.2. *$Te(OH)_6$ – Monoclinic Form (XI)*

The most common form of hexaoxotelluric acid is the monoclinic form with the space group $P2_1/n$ and a = 6.495(1), b = 9.320(1), c = 11.393(1) Å, β = 133.88(1)° (*XIa*, X-ray data[50]). The structure was refined from neutron diffraction data[51] (*XIb*). The intramolecular distances and angles are given in Table I. The structure contains discrete $Te(OH)_6$ octahedra connected by hydrogen bonds, with each molecule involved in twelve such bonds. Density D_x equals 3.067(1) Mg m^{-3} and Z = 4. The infrared data suggest that the monoclinic form is more strongly hydrogen bonded than the cubic form[38,49]. The Mössbauer spectra were studied in refs[32,38] (see β-TeO_3).

7.3. *Te(OH)6 – Tetragonal Form (XII)*

The tetragonal form of hexaoxotelluric acid was prepared by heating the cubic form in dry air in a temperature range of 363 – 383 K (50 h). The cell parameters have been derived from an X-ray single crystal study (a = 15.65(2), c = 15.76(2) Å, ref.[49]), but this form has never been confirmed.

7.4. *Thermal Decomposition of Te(OH)6*

Numerous studies have been conducted on the thermal decomposition of hexaoxotelluric acid[5,30,49,52 – 55]. The course of decomposition is dependent on the experimental conditions. There are two important procedures: the decomposition in air (in a vacuum, in an inert atmosphere) and in a sealed tube.

The following decomposition sequence occurs in air (in a vacuum, in an inert atmosphere).

$$Te(OH)_6 \xrightarrow[-H_2O]{370-450\ K} (H_2TeO_4)_n \cdot (H_2O)_m \xrightarrow[-H_2O,\ -O_2]{520-650\ K} \alpha\text{-}TeO_3 \longrightarrow \gamma\text{-}TeO_3 \xrightarrow[-H_2O,\ -O_2]{690-750\ K}$$

$$Te_2O_5 \xrightarrow[-O_2]{780-820\ K} Te_4O_9 \xrightarrow[-O_2]{830-920\ K} \alpha\text{-}TeO_2 \qquad (A)$$

The following decomposition sequence takes place in a sealed tube (2 cm^3, 0.25 g $Te(OH)_6$).

$$Te(OH)_6 \xrightarrow{410-470\ K} (H_2TeO_4)_3 \cdot (H_2O)_4 \xrightarrow[-H_2O]{570-670\ K} \beta\text{-}TeO_3 \qquad (B)$$

Hexaoxotelluric acid melts when heated in a sealed tube to yield a clear liquid denoted as allotelluric acid $(H_2TeO_4)_3 \cdot (H_2O)_4$ (ref.[56]).

The thermal decomposition of β-TeO_3 in air occurs as follows.

$$\beta\text{-}TeO_3 \xrightarrow[-O_2]{720-780\ K} Te_2O_5 \xrightarrow[-O_2]{810-830\ K} Te_4O_9 \xrightarrow[-O_2]{880-930\ K} \alpha\text{-}TeO_2 \qquad (C)$$

All the temperatures given above are highly dependent on the experimental conditions.

7.5. *Te(OH)$_6$. 4 H$_2$O (XIII)*

The hydrate Te(OH)$_6$. 4 H$_2$O has been prepared at 277 K by slow evaporation from an aqueous solution of Te(OH)$_6$. The crystals are tetragonal with space group $I4_1/a$ and cell parameters a = 10.790 and c = 7.108 Å (ref.[57]).

8. TETRAOXOTELLURIC ACID H_2TeO_4 (*XIV*)

Tetraoxotelluric acid has been prepared by hydrothermal synthesis and belongs to space group $P2_1/c$, a = 5.884(2), b = 4.844(1), c = 5.224(1) Å, β = 116.98(2)° (ref.[58]). The intramolecular distances and angles are given in Table I. The structure contains TeO_6 octahedra which are connected through four corners to form infinite sheets. These sheets are held together by hydrogen bonds. The stoichiometry is described by the formula $[Te(VI)(O_{0.5})_4(OH)_2]_{2\infty}$. Density D_x equals 4.844(1) Mg m^{-3} and Z = 2. The Mössbauer parameter of H_2TeO_4 is very similar to that of β-TeO_3 (ref.[28]). The infrared spectra published in refs[36,59] are not consistent.

9. TELLURIC ACID $H_2Te_2O_6$ (*XV*)

Telluric acid $H_2Te_2O_6$ has been prepared by hydrothermal synthesis and belongs to space group $Pbn2_1$, a = 8.037(5), b = 12.070(5), c = 4.735(5) Å (ref.[60]). The intramolecular distances and angles are given in Table I. The structure contains $Te(VI)O_6$ octahedra and $Te(IV)O_4$ units. The octahedra are linked by four TeO_4 units into infinite sheets which are held together by hydrogen bonds. The stoichiometry is described by the formula $\{[Te(VI)(OH)_2(O^6)_2(O^4)_2][Te(IV)(O^4)_2(O^6)_2]\}_{2\infty}$. Density D_x equals 5.106(1) Mg m^{-3} and Z = 4. The cell parameters, as well as the $H_2Te_2O_6$ structure, are closely related to that of Te_2O_5, in accordance with the formal reaction $H_2Te_2O_6 = Te_2O_5 + H_2O$.

10. ADDITION COMPOUNDS OF HEXAOXOTELLURIC ACID Te(OH)$_6$ (*XVI – LIII*)

Hexaoxotelluric acid Te(OH)$_6$ forms adducts with many kinds of inorganic and organic compounds. Table IV gives the survey of these adducts.

The most studied adduct is telluric acid ammonium phosphate Te(OH)$_6$. 2 $NH_4H_2PO_4$. $(NH_4)_2HPO_4$ (TAAP, *XXIII*). The solubility of TAAP is ≈ 57 g/100 ml water at 293 K. The solubility temperature coefficient is positive. TAAP single crystals weighing up to 50 g have been grown within 80 – 100 days at 298 K under a temperature difference of 2.5 – 3 K. TAAP is monoclinic Pn with the cell dimensions a = 15.66(5), b = 6.314(5), c = 9.818(5) Å, β = 105.49(5)°, Z = 2. The crystal habit is platelike, bounded by important faces {100} < {$\bar{2}$12} < {010} < {100}. Spontaneously nucleated crystals are often contact twins on {101}. The distribution of etch pits indicated that most of the dislocation lines are found in the {$\bar{2}$12} growth sectors. The relative permittivity measure-

TABLE IV
Addition compounds of hexaoxotelluric acid $Te(OH)_6$

No. of compound	Formula[a]	References[b]
XVI	$Te(OH)_6 . 2 KNO_3 . 2 H_2O$	61; I, R, T, D: 62
XVII	$Te(OH)_6 . Na_2HPO_4 . H_2O$	63
	$Te(OH)_6 . Na_2HAsO_4 . H_2O$*	64
XVIII	$Te(OH)_6 . 2 (NH_4)_2HPO_4$	63
	$Te(OH)_6 . 2 (NH_4)_2HAsO_4$*	64
XIX	$Te(OH)_6 . NaH_2PO_4 . Na_2HPO_4$	65
	$Te(OH)_6 . AgH_2PO_4 . Ag_2HPO_4$*	66
	$Te(OH)_6 . NaH_2AsO_4 . Na_2HAsO_4$*	66
	$Te(OH)_6 . AgH_2AsO_4 . Ag_2HAsO_4$*	66
XX	$Te(OH)_6 . RbH_2PO_4 . Rb_2HPO_4$	67
	$Te(OH)_6 . RbH_2AsO_4 . Rb_2HAsO_4$*	64
	$Te(OH)_6 . CsH_2AsO_4 . Cs_2HAsO_4$*	68
XXI	$Te(OH)_6 . Cs_2HPO_4$	69; R, I: 70
XXII	$Te(OH)_6 . 2 CsH_2PO_4 . Cs_2HPO_4$	69
XXIII	$Te(OH)_6 . 2 NH_4H_2PO_4 . (NH_4)_2HPO_4$	71; S: 72; Di: 73, 74; R, I: 75
	$Te(OH)_6 . 2 KH_2PO_4 . K_2HPO_4$*	71; I, R: 76
	$Te(OH)_6 . 2 NH_4H_2AsO_4 . (NH_4)_2HAsO_4$*	71
XXIV	$Te(OH)_6 . 2 Ag_2HPO_4$	77
XXV	$Te(OH)_6 . 2 Tl_2HPO_4$	78
XXVI	$Te(OH)_6 . K_3HP_2O_7 . H_2O$	79
XXVIIa	$Te(OH)_6 . 2 Na_3P_3O_9 . 6 H_2O$	80
XXVIIb		N: 81
XXVIII	$Te(OH)_6 . Na_3P_3O_9 . K_3P_3O_9$	82
XXIX	$Te(OH)_6 . K_3P_3O_9 . 2 H_2O$	83
XXX	$Te(OH)_6 . Rb_3P_3O_9 . H_2O$	84
XXXI	$Te(OH)_6 . Cs_3P_3O_9 . H_2O$	85
XXXII	$Te(OH)_6 . 2 (NH_4)_3P_3O_9$	86
XXXIII	$Te(OH)_6 . K_4P_4O_{12} . 2 H_2O$	87
	$Te(OH)_6 . Rb_4P_4O_{12} . 2 H_2O$*	88
XXXIV	$2 Te(OH)_6 . (NH_4)_4P_4O_{12} . 2 H_2O$	89
XXXV	$2 Te(OH)_6 . K_6P_6O_{18} . 3 H_2O$	90
XXXVI	$3 Te(OH)_6 . Rb_6P_6O_{18} . 4 H_2O$	90
	$3 Te(OH)_6 . Cs_6P_6O_{18} . 4 H_2O$*	90
XXXVII	$Te(OH)_6 . (NH_4)_6P_6O_{18} . 2 H_2O$	91
XXXVIII	$2 Te(OH)_6 . (C_2H_{10}N_2)_3P_6O_{18} . 2 H_2O$	92
XXXIX	$Te(OH)_6 . Na_2SO_4$	93; I, R: 94
XL	$Te(OH)_6 . K_2SO_4$	95; I, R: 96
XLI	$Te(OH)_6 . (NH_4)_2SO_4$	97
XLII	$Te(OH)_6 . Tl_2SO_4$	98; I, R: 94
XLIII	$Te(OH)_6 . (NH_4)_6TeMoO_{24} . 7 H_2O$	99

TABLE IV
(*Continued*)

No. of compound	Formula[a]	References[b]
XLIV	$Te(OH)_6$. NaF	100; I, R: 100
XLV	$Te(OH)_6$. 2 KF	101; I, R: 101
XLVI	$Te(OH)_6$. 2 CsCl	102
XLVII	$Te(OH)_6$. 2 CsF . 2 H_2O	103
XLVIII	$Te(OH)_6$. KIO_3	104
	$Te(OH)_6$. $RbIO_3$*	105
	$Te(OH)_6$. NH_4IO_3*	105
XLIX	$Te(OH)_6$. NH_4IO_3 . H_2O	105
L	$Te(OH)_6$. 2 KIO_3	105
LI	$Te(OH)_6$. 2 $CO(NH_2)_2$	106; D, I, R: 107
LIIa	$Te(OH)_6$. 2 NH_2CH_2COOH . H_2O	120 K: 108
LIIb		293 K: 109; D, I, R: 107
LIIc		N: 110
	$Te(OH)_6$. 2 NH_2CH_2COOH	D, I, R,: 107
LIII	$Te(OH)_6$. 2 (CH_3NHCH_2COOH)	111

[a] Compounds denoted with * are isostructural with the preceding non-denoted. [b] N denotes neutron diffraction data, I infrared spectra, R Raman spectra, T thermal gravimetric analysis, D differential thermal analysis, S single crystal growth and Di dielectic properties.

ments suggest that a ferroelectric or an antiferroelectric transition of near second order occurs at 321 K. Its dielectric properties are anisotropic. The results of microwave dielelctric dispersion confirm the order–disorder nature of a proper ferroelectric phase transition of second order. The pyroelectric field coefficient exhibits a maximum around 308 K, amounting to 10^4 V cm^{-1} K^{-1}. The value of the specific heat C is 1.15 J g^{-1} K^{-1} (2.44 J cm^{-3} K^{-1}) at room temperature. TAAP behaves closely like the triglycine sulfate TGS. The single crystals show hypermorphism. Although they were grown under 321 K, their geometric symmetry belongs to the holoedric point group $2/m$, attributed to the paraelectric phase, instead of the hemihedrical point group m of the ferroelectric phase. The hypermorphism might be explained if it is taken into account that the crystal structure of the ferroelectric phase is close to a centrosymmetric one. Deuterated TAAP, DTAAP, has also been prepared. Deuteration shifts the transition temperature from 318 to 360 K. The broadening of the TAAP bands in the range of 2 600 – 3 400 cm^{-1} suggests the possibility of an order–disorder type of transition phenomenon involving hydrogen bonds. From a practical standpoint, TAAP could be a valuable material for pyroelectric applications because of its superior growth and handling properties (for the references see Table IV).

11. HYDROGEN BONDS

Hydrogen bonding occurs wherever possible in all the compounds with Te(VI)OH formations. The average values of distances and angles of the hydrogen bonds were calculated from the values obtained by neutron diffraction and are given in Table V.

12. DISTORTION INDICES

The DISQ distortion indices according to Baur[112] were used for quantitative evaluation of deviations from the average geometry. The DISQ index (I) is defined by

$$I = \left[\sum_n (T_n - X_n)^2 / \sum_n T_n^2\right] K , \qquad (1)$$

where the values of T_n are the average values of A,B,C,D,E,F (T_{1-6} = 1.915) or A–B,C–D,E–F,A–C,B–E,D–F etc. (T_{1-3} = 178.4, T_{4-15} = 90.0), the values of X_n are the values of the Te–O or O–Te–O under evaluation and K is a constant equal to 10^5 for the distances and 10^4 for the angles. The greater the index value, the more the formation differs from the average values. The DISQ indices are given in Table VI.

13. BOND VALENCES

The bond valences s are calculated from the relationship

$$s = \exp[(r_0 - r)/B] , \qquad (2)$$

where r is an interatomic distance (Å) and r_0 and B are calculated parameters, r_0[Te(IV)–O] = 1.977, r_0[Te(VI)–O] = 1.917 and B = 0.37 (ref.[113]). In an ideal case, $V_i = \sum s_{ij}$, where V_i is the oxidation state of cation i and s_{ij} is the bond valence between cation i and anion j. The j value corresponds to the coordination number. It then holds that the shorter the distance r, the greater is the bond valence expressed in terms of the bond-valence unit. The bond valences are given in Table VII.

14. DISCUSSION

Four-coordinated tellurate(IV) and six-coordinated tellurate(VI) compounds are described in terms of the results found for TeO_2 and $Te(OH)_6$, respectively. Te(IV) is present in a distorted bipyramidal environment. It is bonded to four oxygen atoms and a stereochemically active lone pair is assumed to occupy the fifth coordinate position in the equatorial plane. The lone pair repels the electrons in both the equatorial and the axial bonds, so that the corresponding angles are decreased from the expected values of 180 and 120° to 168(3) and 98(5)°, respectively, see Table I.

TABLE V

Distances (Å) and angles (deg) of hydrogen bonds in $Te(OH)_6$-*c*, $F4_132$ (*Xa*), $Te(OH)_6$-*m*, $P2_1/n$ (*XIb*), $Te(OH)_6 . 2 Na_3P_3O_9 . 6 H_2O$ (*XXVIIb*) and $Te(OH)_6 . 2 NH_2CH_2COOH . H_2O$ (*LIIc*) obtained by neutron diffraction[a]

Compound	*n*	X	Te^d–O^d	O^d–H^d	H^d...O^a	O^a–X^a	Te^d–O^d–H^d	O^d–H^d..O^a	H^d..O^a–X^a	O^d...O^a	Te^d–O^d..O^a	O^d..O^a–Te^a
Xc[b]	3	Te	1.98(1)	0.96(2)	1.65(2)	1.98(1)	113(1)	158(2)	126(1)	2.57(1)	126.6(3)	126.6(3)
				0.96(2)	1.85(2)	1.98(1)	108(1)	171(2)	117(1)	2.80(1)	114.5(3)	114.5(3)
	3	Te	1.81(1)	0.90(2)	1.71(2)	1.81(1)	135(2)	157(2)	118(1)	2.56(1)	125.4(3)	125.4(3)
				0.95(1)	2.10(2)	1.81(1)	122(2)	166(2)	125(1)	3.02(1)	121.5(3)	121.5(3)
Xb	2	Te	1.907(1)	0.986(3)	1.714(3)	1.914(1)	113.6(2)	173.4(3)	125.8(1)	2.696(2)	117.7(1)	123.5(1)
	2	Te	1.908(1)	0.984(3)	1.727(3)	1.909(1)	114.5(2)	175.5(3)	127.5(1)	2.709(2)	116.3(1)	127.6(1)
	2	Te	1.910(1)	0.978(3)	1.720(3)	1.908(1)	114.2(2)	175.7(3)	126.2(1)	2.696(2)	115.5(1)	125.6(1)
	2	Te	1.909(1)	0.989(3)	1.699(3)	1.910(1)	113.1(2)	174.5(2)	127.7(1)	2.685(2)	116.5(1)	125.7(1)
	2	Te	1.908(1)	0.986(3)	1.704(3)	1.908(1)	114.9(2)	167.1(3)	129.5(1)	2.675(2)	121.0(1)	128.5(1)
	2	Te	1.914(1)	0.981(3)	1.750(3)	1.907(1)	112.6(2)	175.2(3)	129.6(1)	2.729(2)	113.4(1)	128.8(1)
XXVIIb	6	P	1.95(1)	0.84(2)	1.86(2)	1.48(1)	109(1)	163(6)	140(1)	2.67(1)		
LIIc	2	C	1.916(1)	0.99(1)	1.64(1)	1.249(6)	113(1)	172.2(9)	123(1)	2.626(7)		
	2	C	1.923(4)	1.018(9)	1.61(1)	1.269(6)	112(1)	171.0(8)	117(1)	2.624(6)		
	2	C	1.925(4)	0.99(1)	1.78(1)	1.269(6)	115(1)	166.4(8)	125(1)	2.748(7)		
				N^d–H^d	H^d...O^a	O^a–Te^a		N^d–H^d–O^a	H^d–O^a–Te^a	N^d...O^a		
	2	Te		1.03(1)	1.98(1)	1.925(4)		162.8(9)	118(1)	2.979(7)		
Mean values of Te–O–H...O–Te (*n* = 18)			1.90(5)	0.97(2)	1.8(1)	1.90(5)	116(7)	170(6)	126(4)	2.7(1)	118(4)	125(4)

[a] *n* Denotes number of distances or angles in the $Te(OH)_6$ formations, superscripts d and a denote donor and acceptor atoms. [b] Multiplicity factor of H-atoms in compound *Xc* is 0.5.

The Te(IV) electron distribution may be represented as three sp^2 hybridized orbitals (corresponding to two strong bonds and a lone electron pair in the equatorial directions in a trigonal bipyramid) and one *pd* orbital (corresponding to the weaker bonds in the axial directions).

In TeO_6, all the valency shell electrons are used in σ bonding. An octahedral arrangement with the sp^3d^2 hybridization follows from these.

With regard to the DISQ distortion indices, the $Te(OH)_6$ formations are virtually regular, as only two formations of 54 exceed the value $\bar{x} + \sigma = 42$ for the Te(VI)–O distances and four formations exceed the value $\bar{x} + \sigma = 10$ for the O–Te(VI)–O angles. With regard to the Σs (Te(IV)–O) criterion, only 4 formations exceed the values $\bar{x} \pm \sigma = 6.23$ or 5.87, respectively.

The average Σs(Te(IV)–O) value given in Table VII is primarily affected by the value calculated for γ-TeO_2 (*III*). This value suggests that structure *III* has been determined with a precision poorer than for structures *I* and *II*. When this value is excluded, the arithmetic mean increases to 3.94(10), which is closer to the theoretical value 4.

TABLE VI
DISQ distortion indices for Te(VI)–O(H) distances ($K = 10^5$) and O(H)–Te(VI)–O(H) angles ($K = 10^4$), $n = 54$

Parameter	Distances			Angles		
	minimum	average	maximum	minimum	average	maximum
Value	0.1	11(31)	207	0.4	4(6)	37
Compound	*Xa*		*Xc*	*Xa*		*XLI*

TABLE VII
Σs(Te–O) values in $Te(IV)O_4$ and $Te(VI)O_6$ formations

Formation	*n*	Σs(Te–O)		
		minimum	average	maximum
$Te(IV)O_4$	6	3.61	3.89(17)	4.04
Compound		*III*		*IV*
$Te(VI)O_6$	59	5.53	6.05(18)	7.06
Compound		*XXVIIb*		*XLVII*

Considering the paramagnetic products γ-TeO_3 (*IX*) it is interesting e. g. the products obtained by heating CeO_2 in a vacuo at temperatures of 573 – 1 073 K exhibit ESR signals believed to be due to O_2^- (g_n = 2.008 – 2.047). These products also change their colour from bright yellow to pale blue to darker blue[114].

It should be pointed out that in all the three compounds (*IV*, *V*, *XV*), in which atoms of both tetra- and hexavalent tellurium occur and whose structures are known, the O(a) and O(d) oxygen atom are always still bound to Te(VI) atoms, whereas O(b), O(c) and O(A) atoms are bound to Te(IV) atoms. The reason for this is unclear.

Reference[46] gives, on the structure of cubic modification of hexaoxotelluric acid $Te(OH)_6$ (*Xc*) the value of one angle, Te–O–H = 118(2)°. However, this value is incorrect and should be 135(2)°, i.e. should exceed the value $\bar{x} + 3\sigma = 132°$. The Te–O = 1.81(1) Å distances also lie at the limit of the value, $\bar{x} - 3\sigma = 1.80$ Å. As the DISQ value for distances 207 also considerably exceeds the value, $\bar{x} + 3\sigma = 103$, this structure is dubious.

It seems that the structure of substance *XLI* should be checked, in view of the DISQ value for the angles 37. The same holds for substance *XLVII* and the value Σs(Te(VI)–O) = 7.1.

The Te(VI)–O(A,B,C,D,E,F) distances and the corresponding O–Te(VI)–O angles are not statistically different. No correlation has been found between the Te–O distances and O–Te–O angles. The average distances and angles Te(IV)–O–Te(IV), Te(IV)–O–Te(VI) and Te(VI)–O–Te(VI) are 1.90(5), 2.11(4) Å and 128(11)° (n = 18), 1.97(7), 1.91(3) Å and 134(6)° (n = 10) and 1.92(1), 1.93(2) Å and 136(1)° (n = 16).

The average distance of the $O^d...O^a$ hydrogen bond (superscripts d and a denote donor and acceptor, respectively), 2.7(1) Å corresponds to the bond valence $s(H^d...O^a)$ = 0.20. This value is equal to the value calculated for the distance $H^d...O^a$ = 1.8(1) Å (see Table V) and corresponds to a relatively strong hydrogen bond.

The stability of the $Te(OH)_6$ formation in addition compounds is interesting. All the compounds studied have been obtained from aqueous solutions and none of them contains a dissociated form of hexaoxotelluric acid, e.g. $Te(OH)_5O^-$ etc. The reason apparently lies in the fact that the $Te(OH)_6$ is very weak acid in water ($K_1 = 2.0 \cdot 10^{-8}$, $K_2 = 1 \cdot 10^{-11}$, $K_3 \approx 3 \cdot 10^{-15}$, ref.[1]) and the charges on the cations are compensated for by the charges on the anions of stronger acids.

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