The Crystal Structure of Ditellurium Pentoxide, Te₂O₅

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Single crystals of Te_2O_5 have been prepared by hydrothermal synthesis and the crystal structure has been determined from three-dimensional X-ray data. The crystals are monoclinic, space group $P2_1$, with $a = 5\cdot368$, $b = 4\cdot696$, $c = 7\cdot955$ Å, $\beta = 104\cdot82°$ and $Z = 2$. The atomic positions were obtained from Patterson and electron-density summations and the structure was refined to an R value of $0\cdot040$ using 2205 independent reflexions. Te_2O_5 contains octahedrally coordinated tellurium(VI) and four-coordinated tellurium(IV) atoms, with Te(VI)–O and Te(IV)–O distances in the ranges $1\cdot848–1\cdot972$ Å and $1\cdot892–2\cdot080$ Å respectively. The $Te(VI)O_6$ octahedra are connected through corners to form infinite sheets of composition $[Te(VI)O_4]_n^{2n-}$, between which $[Te(IV)O]_n^{2n+}$ chains run. Related compounds of composition $H_2Te_2O_6$ and Te_4O_9 are under investigation.

Introduction

The three-dimensional structure of paratellurite, α-TeO_2, has been known since the work of Stehlik & Balák (1949), and the structural parameters have been refined in later investigations (Leciejewicz, 1961; Lindqvist, 1968). The structure of tellurite, α-TeO_2, has also been determined (Beyer, Zahl & Zemann, 1965; Beyer, 1967). A powder investigation of a modification of the trioxide, β-TeO_3, has indicated that this structure is of the TiF_3 type (Dumora & Hagenmuller, 1968).

During the last few years other tellurium oxides have been described in the literature. Breusov, Vorobeva, Druz, Revzina & Sobolev (1966) obtained a number of different phases through thermal decomposition of $Te(OH)_6$. However, it appears that these compounds did not give rise to well characterized powder diagrams. Rosicky, Loub & Pavel (1965) have described a method of preparing a phase of composition Te_2O_5. Another modification of Te_2O_5, showing a different powder diagram, has been synthetized by Moret & Maurin (1968), through thermal decomposition of TeO_3 or $(TeO_3.H_2O)_n$ obtained by hydrothermal synthesis.

Since the oxidation state of tellurium in Te_2O_5 is formally $+V$, it is of interest to determine the configuration of the oxygen atoms around tellurium and thus clarify the Te valence in this compound. The aim of this investigation was therefore to devise a method of preparing single crystals of Te_2O_5 and to make a three-dimensional X-ray structure determination.

Experimental

Preparation of the crystals

No noticeable dissolution of Te_2O_5, obtained by the thermal decomposition of TeO_3 or $(TeO_3.H_2O)_n$, was achieved with ordinary solvents (HCl, *etc.*) at atmospheric pressure. On the other hand, tellurium oxides and hydroxides, such as TeO_2 (Glemser, Müller & Schwarzkopf, 1965), Te_2O_5, TeO_3 and H_2TeO_4 dissolve readily under pressure in a number of solvents, and particularly in pure water, *i.e.* hydrothermal synthesis appeared to be a suitable method for the preparation of single crystals of Te_2O_5 (Laudise & Nielsen, 1961).

In this investigation the solubilities of TeO_2, Te_2O_5 and TeO_3 in water were studied qualitatively in the pressure and temperature ranges 1–1000 bar and 25–450 °C respectively. The results made it possible to define conditions under which crystalline Te_2O_5 will form. Crystals suitable for an X-ray single-crystal investigation formed, together with small amounts of TeO_3, when $0\cdot8$ g $Te(OH)_6 + 2$ g H_2O were kept in a temperature gradient autoclave of the Bridgman type (*cf.* Moret, 1972) for five days. The temperature gradient was 50 °C and the average temperature in the bomb was approximately 370 °C. The corresponding pressure was calculated (Kennedy, 1950) to be approximately 900 bar.

A method for the preparation of pure, microcrystalline Te O₅ has also been devised, and a detailed description of this synthesis is given elsewhere (Moret, 1972).

Analysis

The tellurium content was determined gravimetrically to be 76 % (Moret & Maurin, 1968). The product was converted to paratellurite by heating to 600 °C. The result obtained by weighting the paratellurite was checked by reducing the tellurium to Te^0 with $CH_2N_2.HCl + SO_2$ (Charlot, 1961).

The oxygen content was determined thermogravi-

metrically to be 24%, and the absence of water was verified with I.R. spectroscopic methods.

The results of the analyses indicate the formula to be Te_2O_5, the uncertainity in these determinations being approximately $\pm 2\%$. That the formula is in fact Te_2O_5 is confirmed by the results of the X-ray investigation.

The density, determined with a pychnometer, was found to be $5\cdot7$ g cm^{-3}.

Unit cell and space group

From Weissenberg films it could be seen that Te_2O_5 crystallizes in the monoclinic system. The only system-

atic absences occurred among the $0k0$ reflexions for $k = 2n + 1$, indicating the space group to be either $P2_1$ or $P2_1/m$.

The cell dimensions were determined from measure-

Table 2. *Dimensions of the crystal*

The distances from a common origin to each plane are given.

Plane h k l	d (mm)
0 1 0	0·215
0 1̄ 0	0·215
1 0 0	0·050
1 1 0	0·037
0 0 1	0·022
1̄ 0 0	0·044
1̄ 1̄ 0	0·036
0 0 1̄	0·022

Crystal volume: $0\cdot42.10^{-3}$ mm³

Fig. 1. Coordination of the 6-valent tellurium (probability level: 50%).

Table 1. *Powder data and cell dimensions for* Te_2O_5

h k l	sin² θ (obs)	sin² θ (calc)	d(calc) Å	I
0 0 1	0·01004	0·01003	7·691	m
1 0 0	0·02205	0·02203	5·190	m
0 1 1	0·03688	0·03694	4·008	s
1 0 1	0·03955	0·03966	3·868	s
0 0 2	0·04009	0·04012	3·845	s
1̄ 0 2	0·04707	0·04695	3·555	w
1 1 0	0·04893	0·04894	3·482	s
1̄ 1 1	0·05141	0·05137	3·399	vs
1 1 1	0·06655	0·06657	2·985	s
0 1 2	0·06699	0·06703	2·975	s
1̄ 1 2	0·07377	0·07386	2·834	m
1 0 2	0·07729	0·07736	2·769	w
2 0 0	0·08804	0·08812	2·595	m
1̄ 0 3	0·08943	0·08950	2·575	m
0 0 3	0·09013	0·09028	2·564	m
2̄ 0 2	0·09776	0·09783	2·463	s
1 1 2	0·10428	0·10427	2·385	s
0 2 0	0·10761	0·10763	2·348	m
2̄ 1 1	0·10979	0·10985	2·324	w
2 0 1	0·11341	0·11346	2·268	m
2 1 0	0·11497	0·11503	2·271	m
1̄ 1 3	0·11630	0·11641	2·258	m
0 2 1	0·11754	0·11766	2·245	m
2̄ 1 2	0·12482	0·12474	2·181	w
1 2 0	0·12960	0·12966	2·139	w
1 0 3	0·13492	0·13512	2·095	w
2 1 1	0·14033	0·14026	2·057	m
0 2 2	0·14769	0·14776	2·004	m
1̄ 0 4	0·15217	0·15211	1·975	m
1̄ 2 2	0·15456	0·15458	1·959	w
2̄ 1 3	0·15964	0·15969	1·928	m
1 1 3	0·16207	0·16203	1·914	m
1̄ 1 4	0·17888	0·17903	1·820	w
1 2 2	0·18507	0·18499	1·791	m
3̄ 0 1	0·18547	0·18549	1·788	w
2̄ 0 4	0·18793	0·18779	1·777	w
2̄ 2 1	0·19066	0·19058	1·764	w
2 2 0	0·19575	0·19575	1·741	m
0 2 3	0·19798	0·19791	1·731	m
2̄ 2 2	0·20540	0·20546	1·699	m
3̄ 1 1	0·21249	0·21240	1·671	m
2̄ 1 4	0·21465	0·21470	1·662	m
2 2 1	0·22099	0·22099	1·639	m
2 0 3	0·22403	0·22402	1·627	m
3 1 0	0·22490	0·22518	1·623	m
2̄ 2 3	0·24024	0·24041	1·571	m
3̄ 1 3	0·24698	0·24703	1·550	m
0 0 5	0·25076	0·25077	1·538	m

Cell dimensions: $a = 5\cdot3680$ (7) Å $U = 193\cdot85$ (5) Å³
$b = 4\cdot6959$ (8) $Z = 2$
$c = 7\cdot9551$ (11)
$\beta = 104\cdot82$ (1)°
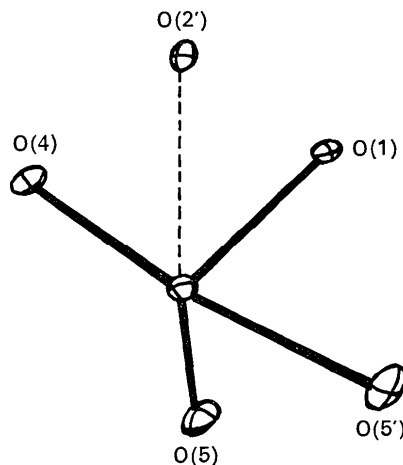

Fig. 2. Coordination of the 4-valent tellurium (probability level: 50%).

ments on a Siemens powder diffractometer calibrated with a gold sample, the refinement being performed with the program *POWDER* (Lindqvist & Wengelin, 1967). The powder data and the cell dimensions are given in Table 1.

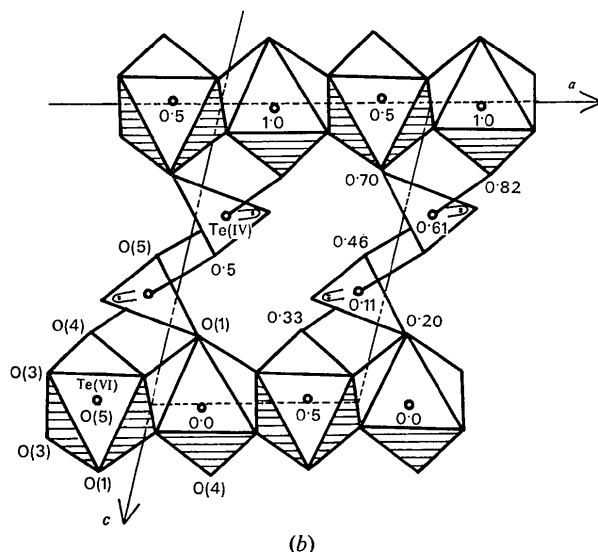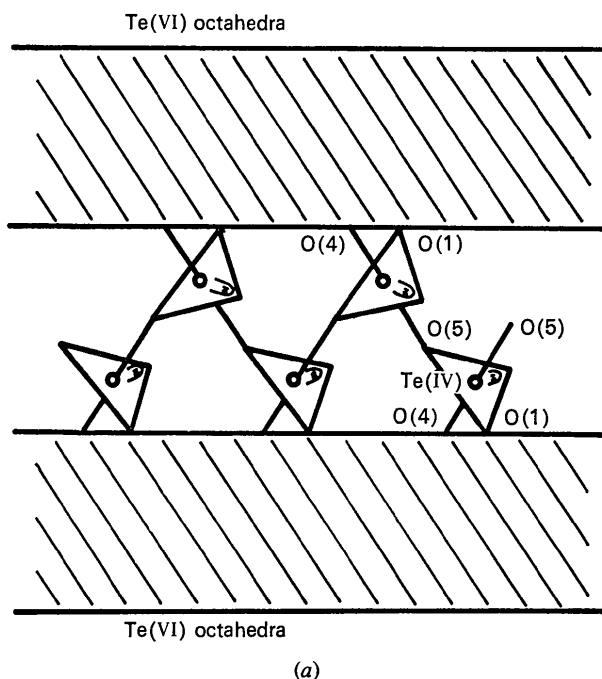Assuming that $Z=2$, the calculated density of Te_2O_5

Te(VI) octahedra

(a)

(b)

Fig. 3. Schematic projections along the crystallographic axes. (a) Projection along the a axis showing part of a Te(IV) chain. (b) Projection along the b axis indicating the channels in the structure. In (a) and (b) the Te(IV) lone pair is indicated in an equatorial position in the Te(IV) trigonal bipyramid coordination polyhedron.
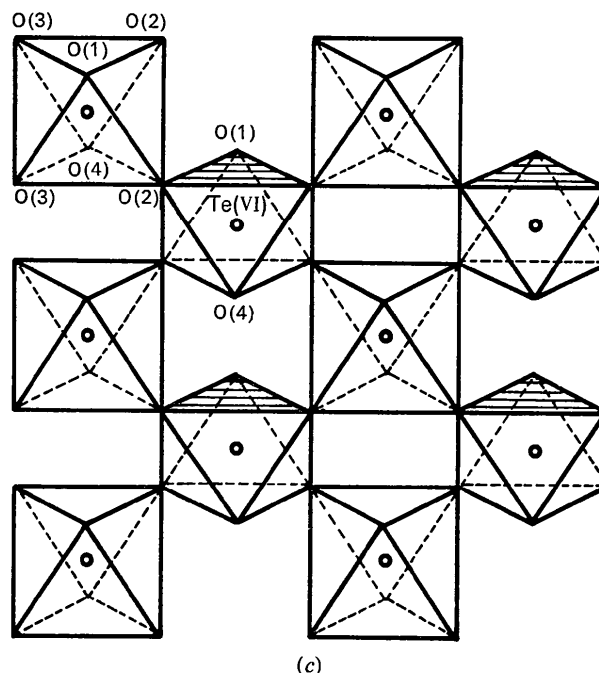
(c)

Fig. 3 (*cont.*). (c) Projection along the c axis showing one Te(VI) plane.

is 5.735 g cm^{-3}, which is in good agreement with the experimental value.

Intensity data

Three-dimensional X-ray data were collected with a Philips PAILRED single-crystal diffractometer (equi-inclination Weissenberg geometry). A single crystal of the dimensions given in Table 2 was mounted along the b axis, and 2278 independent reflexions on the layers $h0l–h8l$ ($l \geq 0$) were recorded with graphite mono-chromated Mo $K\alpha$ radiation and a scintillation counter. The ω-scan technique was used with a scan speed of $2.5°$ per min, and the background for each reflexion was measured for 40 sec at each end of the scan interval.

The intensities were processed using the program *DATAP* 1. Standard deviations, $\sigma(I)$, based on counting statistics, were evaluated, and those reflexions with

Table 3. *Final atomic parameters for* Te_2O_5

The anisotropic temperature factor is

$$\exp\left[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + hka^*b^*U_{12} + hla^*c^*U_{13} + klb^*c^*U_{23}) \times 10^{-4}\right].$$

Standard deviations are given in parentheses.

	x	y	z	$B(\text{Å}^2)$
Te(VI)	0·25722 (5)	0	0·01238 (4)	0·344 (7)
Te(IV)	0·14156 (6)	0·61299 (9)	0·38171 (4)	0·541 (7)
O(1)	0·1635 (8)	0·2039 (10)	0·7948 (5)	0·54 (4)
O(2)	0·0377 (8)	0·2705 (10)	0·0988 (6)	0·61 (5)
O(3)	0·5355 (9)	0·2659 (11)	0·0935 (6)	0·67 (5)
O(4)	0·6607 (10)	0·3273 (11)	0·7717 (6)	0·76 (6)
O(5)	0·8713 (11)	0·4679 (13)	0·5082 (7)	1·00 (7)

Table 3 (cont.)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te(VI)	44 (1)	37 (1)	51 (1)	2 (1)	32 (1)	2 (1)
Te(IV)	75 (1)	76 (1)	60 (1)	23 (1)	37 (1)	5 (1)
O(1)	79 (11)	82 (13)	56 (11)	−7 (19)	43 (17)	37 (18)
O(2)	69 (11)	84 (14)	83 (13)	78 (19)	38 (18)	−12 (19)
O(3)	102 (13)	94 (15)	76 (13)	−94 (22)	47 (20)	2 (20)
O(4)	126 (14)	93 (15)	65 (13)	−27 (22)	86 (21)	−58 (20)
O(5)	145 (17)	130 (20)	143 (17)	80 (27)	152 (27)	148 (27)

$\sigma(I)/I \leq 0.4$ were regarded as observed. Only 73 of the 2278 measured reflexions did not fulfil this condition. Corrections for Lorentz and polarization effects were calculated with the same program.

The absorption coefficient, $\mu(\text{Mo } K\alpha) = 151.6 \text{ cm}^{-1}$, was calculated from the elementary values given in *International Tables for X-ray Crystallography* (1962), and the absorption factors were evaluated with the program *DATAP2*. The crystal (*cf.* Table 2) was divided into $6 \times 8 \times 4$ Gaussian grid points along the *a, b* and *c* axes respectively, and the resulting transmission values varied between 0.35 and 0.58.

Solution and refinement of the structure

A three-dimensional Patterson summation was calculated with the data as yet uncorrected for absorption effects. The tellurium–tellurium interatomic vectors could not be interpreted in agreement with vector sets possible in space group $P2_1/m$, while they could be readily shown to correspond to two twofold positions in the acentric space group $P2_1$. A subsequent difference electron-density calculation revealed all the oxygen atoms in the structure. The Fourier summations were performed with the program *DRF*.

Table 4. *Observed and calculated structure factors*

The columns are h, F_o, $|F_c|$ and φ (in radians) respectively. Unobserved reflexions are indicated with an asterisk.

Table 4 (cont.)

Table 4 (cont.)

A preliminary refinement of the atomic positions and isotropic temperature factors gave an R value of 0·10 ($R = \sum|F_o - |F_c||/\sum F_o$). After having introduced the correction for absorption, the isotropic refinement was repeated, including refinement of an isotropic secondary extinction factor and separate scale factors for each layer. The R value dropped to 0·053; the corresponding isotropic temperature factors are given in Table 3. None of the interlayer scale factors deviated significantly from the average value, the largest deviation being 2·5%.

The final refinement was extended to include anisotropic thermal parameters, the scale factors for each layer being kept constant. The R value converged to 0·040; the final parameters are given in Table 3. The

observed and calculated structure factors are compared in Table 4.

All refinement was performed with the program *LINUS*, which handles refinement of secondary-extinction parameters. The diffraction from the crystal of Te_2O_5 used was associated with appreciable extinction effects, and the final value of the isotropic extinc-

Table 5. *Weight analysis after the final cycle of refinement*

The quantities wA^2 are normalized sums, $K_{norm} \cdot (\sum w|F_o - |F_c||^2)$, and N is the number of reflexions within each F_o interval.

F_o interval	N	wA^2
0·0–10·0	206	1·77
10·0–15·0	285	1·04
15·0–18·0	190	0·79
18·0–22·0	267	0·92
22·0–27·0	294	0·80
27·0–31·0	198	0·81
31·0–35·0	164	0·96
35·0–43·0	228	0·73
43·0–56·0	198	0·96
56·0–	175	1·37

$$R = \sum|F_o - |F_c||/\sum F_o = 0{\cdot}040$$
$$R_w = [\sum(w|F_o - |F_c||^2)/\sum wF_o^2]^{1/2} = 0{\cdot}057$$

Table 6. *Distances and angles with the tellurium–oxygen polyhedra*

The notation is in accordance with Figs. 1 and 2.

Te(VI)–O(1)	1·929 (4) Å	Te(IV)–O(1)	1·913 (4) Å
Te(VI)–O(2)	1·933 (4)	Te(IV)–O(2′)	2·706 (4)
Te(VI)–O(2′)	1·972 (4)	Te(IV)–O(4)	2·072 (5)
Te(VI)–O(3)	1·907 (5)	Te(IV)–O(5)	1·892 (6)
Te(VI)–O(3′)	1·927 (5)	Te(IV)–O(5′)	2·080 (6)
Te(VI)–O(4)	1·848 (4)		
		O(1)–Te(IV)–O(2′)	64·3 (2)°
O(1)–Te(VI)–O(2)	82·6 (2)°	O(1)–Te(IV)–O(4)	86·0 (2)
O(1)–Te(VI)–O(2′)	87·2 (2)	O(1)–Te(IV)–O(5)	91·0 (2)
O(1)–Te(VI)–O(3)	86·4 (2)	O(1)–Te(IV)–O(5′)	81·8 (2)
O(1)–Te(VI)–O(3′)	88·9 (2)	O(2′)–Te(IV)–O(4)	80·0 (2)
O(1)–Te(VI)–O(4)	175·9 (2)	O(2′)–Te(IV)–O(5)	152·2 (2)
O(2)–Te(VI)–O(2′)	91·5 (1)	O(2′)–Te(IV)–O(5′)	100·8 (2)
O(2)–Te(VI)–O(3)	88·8 (2)	O(4)–Te(IV)–O(5)	86·0 (2)
O(2)–Te(VI)–O(3′)	171·4 (2)	O(4)–Te(IV)–O(5′)	165·9 (2)
O(2)–Te(VI)–O(4)	98·8 (2)	O(5)–Te(IV)–O(5′)	87·3 (2)
O(2′)–Te(VI)–O(3)	173·5 (2)		
O(2′)–Te(VI)–O(3′)	87·0 (2)	Te(IV)–O(1)–Te(VI)	121·7 (2)
O(2′)–Te(VI)–O(4)	88·9 (2)	Te(IV)–O(2′)–Te(VI)	131·2 (2)
O(3)–Te(VI)–O(3′)	91·8 (1)	Te(IV)–O(2′)–Te(VI′)	91·1 (2)
O(3)–Te(VI)–O(4)	97·5 (2)	Te(IV)–O(4)–Te(VI)	136·4 (3)
O(4)–Te(VI)–O(3′)	89·6 (2)	Te(IV)–O(5)–Te(IV)	128·7 (3)
Te(VI)–O(2)–Te(VI)	133·8 (2)		
Te(VI)–O(3)–Te(VI)	135·7 (2)		

tion parameter (Coppens & Hamilton, 1970) was $g \cdot 10^{-4} = 2·24 \pm 0·05$.

The atomic scattering factors used in the refinement were those given by Cromer & Waber (1965), corrected for anomalous scattering (Cromer, 1965) for Te, and those devised by Doyle & Turner (1968) for O. Weights calculated with the formula $w = (25·0 + F_o + 0·02F_o^2)^{-1}$ were found to give reasonable results (cf. Table 5).

Interatomic distances and angles were calculated with the program *DISTAN* and the results are given in Tables 6 and 7.

All computations were performed on an IBM 360/65 computer, using the program library of the Department of Inorganic Chemistry, Göteborg. *DATAP*1 has been written locally by O. Lindgren, *DATAP*2 was originally written by Coppens, Leiserowitz & Rabinovich (1965), and *DRF* and *DISTAN* by A. Zalkin, Berkeley, California. *LINUS* is the Busing, Martin & Levy (1962) least-squares program modified for refinement of extinction parameters (Coppens & Hamilton, 1970).

Table 7. *Oxygen–oxygen distances less than* 3·4 Å

The position of atom 1 is in accordance with Table 3. For atom 2, a superscript (i) indicates a screw-axis operation; translations along the *a*, *b*, and *c* axes are given in the last column.

Atom 1	Atom 2	d (Å)	Translation		
O(1)	···O(2)	2·690 (6)	0	0	1
O(1)	···O(2^i)	2·548 (7)	0	−1	1
O(1)	···O(2^i)	3·071 (7)	0	0	1
O(1)	···O(3)	2·700 (6)	0	0	1
O(1)	···O(3^i)	2·626 (7)	1	−1	1
O(1)	···O(3^i)	3·103 (7)	1	0	1
O(1)	···O(4)	2·720 (6)	−1	0	0
O(1)	···O(4)	2·783 (6)	1	0	0
O(1)	···O(5)	2·714 (7)	−1	0	0
O(1)	···O(5)	2·616 (7)	0	−1	1
O(2)	···O(2^i)	2·797 (5)	0	−1	0
O(2)	···O(2^i)	2·797 (5)	0	0	0
O(2)	···O(3)	2·686 (6)	−1	0	0
O(2)	···O(3)	2·683 (6)	0	0	0
O(2)	···O(4)	2·872 (6)	−1	0	−1
O(2)	···O(4^i)	2·676 (7)	1	−1	1
O(2)	···O(4^i)	3·109 (7)	1	0	1
O(3)	···O(3^i)	2·753 (5)	1	−1	0
O(3)	···O(3^i)	2·753 (5)	1	0	0
O(3)	···O(4)	2·823 (6)	0	0	−1
O(3)	···O(4^i)	2·661 (7)	1	−1	1
O(3)	···O(4^i)	3·128 (7)	1	0	1
O(4)	···O(5)	2·706 (7)	0	0	0
O(5)	···O(5^i)	2·744 (6)	2	−1	1
O(5)	···O(5^i)	2·744 (6)	2	0	1

Discussion

The oxygen coordination of the tellurium atoms in the structure provides clear evidence that Te$_2$O$_5$ contains both 4- and 6-valent tellurium. Te(VI) has the usual octahedral coordination (cf. Fig. 1 and Table 6) found, for example, in Te(OH)$_6$ (Lindqvist, 1970), while the coordination of Te(IV) is irregular fourfold (cf. Fig. 2 and Table 6), and is rather similar to the Te–O configuration in α-TeO$_2$ (Leciejewicz, 1961; Lindqvist, 1968) and in β-TeO$_2$ (Beyer, 1967).

Each Te(VI) octahedron shares corners with four other octahedra, resulting in [Te(VI)O$_4$]$_n^{2n-}$ layers stretching through the structure, as indicated in Fig. 3(c). In KTeO$_3$(OH), which also has a Te(VI):O ratio of 1:4, there are no such layers but the octahedra share edges to form infinite chains (Lammers, 1964; Lindqvist, 1973). Similar structural arrangements have been found for the infinite [UO$_2$O$_2$]$_n^{2n-}$ ions (Zachariasen, 1954b), which, in the compound BaUO$_2$O$_2$, extend to infinite layers as in Te$_2$O$_5$ (Samson & Sillén, 1947), while in MgUO$_2$O$_2$ chains are present as in KTeO$_3$(OH) (Zachariasen, 1954a).

Between the octahedral layers, which can be formu-

lated as $[Te(VI)O_4]_n^{2n-}$, there are chains of $[Te(IV)O]_n^{2n+}$ parallel to the a axis [Figs. 3(a), (b)]. Since all non-bridging oxygen atoms in the $[Te(VI)O_4]_n^{2n-}$ layers are also bonded to the Te(IV) atoms, a three-dimensional covalent net is formed. A stereoscopic projection (Johnson, 1965) of parts of one Te(VI) layer and one Te(IV) chain is shown in Fig. 4. Between the layers and chains there are rather wide channels [Fig. 3(b)]. However, the Te(IV) lone pairs are directed towards the interior of these channels, and the free space is therefore limited, since a Te(IV) lone pair requires a space comparable with that of an oxygen anion (Åström, 1972).

The Te–O bond distances in the Te(VI) octahedron range from 1·848 Å to 1·972 Å (Table 6) with a mean value of 1·919 (2) Å. This value compares quite well with the average Te–O distance of 1·916 (3) Å found in $Te(OH)_6$ (Lindqvist, 1970). Since there is no significant difference between any of the six crystallographically independent Te–O bond lengths in $Te(OH)_6$, the value 1·919 (3) Å may be regarded as being the length of an unaffected Te–O octahedral σ–π bond. In a more recent neutron-diffraction study of $Te(OH)_6$ (Lindqvist & Lehmann, 1973) no significant differences among the six Te–O bonds were found, but a slightly lower average of 1·909 (1) Å was obtained. Although this value is more precise, the X-ray result should be used when discussing Te–O octahedral bonds obtained in X-ray investigations. In Te_2O_5 some of the bond lengths differ significantly from the average values in both Te_2O_5 and $Te(OH)_6$. These deviations can possibly be used to obtain a qualitative estimate of the bond strength of the Te(IV)–O bonds in Te_2O_5.

The four-coordinated Te(IV) atom has a fifth oxygen atom, O(2′), at a distance of 2·706 (4) Å. Similar distances have been found in a number of Te(IV) compounds (Zemann, 1971). In Te-catecholate this fifth distance, 2·64 Å, was claimed to represent a weak intermolecular Te(IV)–O bond (Lindqvist, 1967). In Te_2O_5 both O(2) and O(3) bridge two Te(VI) atoms. The fact that the average Te(VI)–O(2) bond (1·953 Å) is longer than the corresponding value for Te(VI)–O(3) (1·917 Å) indicates an interaction between Te(IV) and O(2′). The geometrical arrangement of the atoms (Fig. 5) also makes the difference between the Te(VI)–O(2′) and the Te(VI′)–O(2′) bond lengths plausible. Moreover, it is quite reasonable that the shorter Te(VI)–O(3) bond of 1·907 Å is opposite to the longer Te(VI)–O(2′) bond of 1·972 Å, assuming the Te(VI) bonding system to be based on the $5p$ orbitals.

The Te(IV) electron distribution may be represented as three sp^2 hybridized orbitals (corresponding to a free electron pair and two strong bonds – 'equatorial' directions in a trigonal bipyramid), and one $5p_z$ orbital (corresponding to the two weaker bonds – 'axial' directions). This representation has been suggested by Lindqvist (1967) and by Meunier & Galy (1971). The weaker character of the Te(IV)–O 'axial' bonds is demonstrated by a comparison between the octahedral Te(VI)–O(1) and Te(VI)–O(4) bonds, the first of which is slightly longer than the expected octahedral Te–O σ–π bond, while the latter is appreciably shorter. The only apparent difference between O(1) and O(4) is that O(1) is 'equatorially' bonded and that O(4) is 'axially' bonded to Te(IV). The 'axial' Te(IV)–O(4) bond is not elongated [cf. Table 1 given by Zemann (1971)] as a consequence of the strong Te(VI)–O(4) bond (1·848 Å). However, it might be referred to as weak in the sense that it seems to be a pure σ single bond, the remaining O(4) orbitals being left free to combine in the most profitable way with the Te(VI) orbital system. Since this is not the case for the other oxygen atoms in the Te(VI) octahedron, the Te(VI)–O(4) σ–π bond ought to have a much higher than average π-bond order. This would account for the fact that the Te(VI)–O(4) bond is even as short or shorter than the Te–O 'keto' bond, which has been found to lie in the range 1·83–1·91 Å in water soluble tellurates, such as $KTeO(OH)_5 . H_2O$ (Raman, 1964), $K_4[Te_2O_6(OH)_4] . (H_2O)_{7·3}$ (Lindqvist & Lundgren, 1966) and $Na_2K_4[Te_2O_8(OH)_2] . (H_2O)_{14}$ (Lindqvist, 1969).
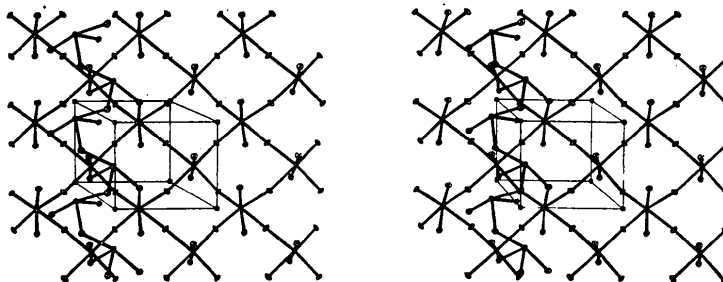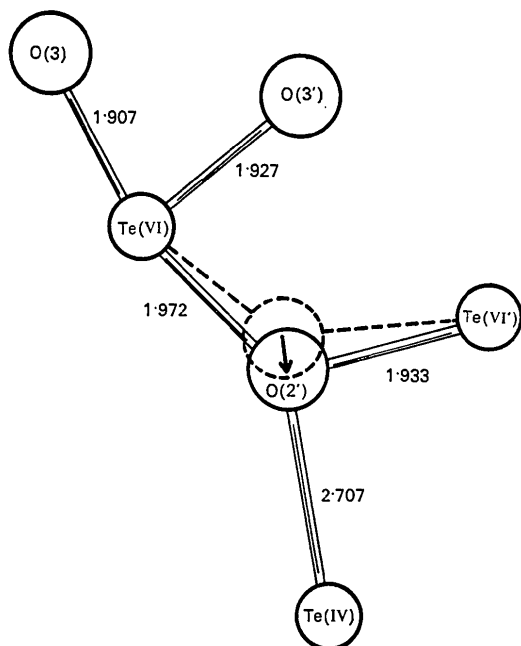
Fig. 4. Stereoscopic view drawn with the program *ORTEP* (Johnson, 1965).

Fig. 5. An illustration of the assumed Te(IV)–O(2′) interaction.

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