

A Neutron Diffraction Refinement of the Crystal Structure of Telluric Acid, $\text{Te}(\text{OH})_6(\text{mon})$

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A neutron diffraction analysis of the monoclinic modification of telluric acid has been carried out in order to obtain the hydrogen positions with high precision and accuracy, thus complementing the earlier X-ray work. Full matrix least squares refinement based on 591 observed reflections gave a final R value of 0.024.

The Te—O and O—H bonds have been determined with a precision of 0.001 and 0.003 Å, respectively. The O—H bonds range from 0.977 to 0.990 Å, with a mean value of 0.985 Å. The mean O—H...O angle in the hydrogen bonds is 173.6°.

The scattering length of tellurium was refined to the value $b_{\text{Te}} = 5.80 \pm 0.05$ F, to be compared with 5.6 F given by The Neutron Diffraction Commission.

The crystal structure of the monoclinic modification of telluric acid, $\text{Te}(\text{OH})_6(\text{mon})$, has recently been determined by Lindqvist¹ using X-ray diffraction methods. Owing to the fact that the tellurium atoms did not contribute to more than one quarter of the possible reflections, five of the six independent hydrogen positions in the unit cell could be located from electron density calculations. However, the precision of the hydrogen parameters was not high, and in order to obtain more information concerning the hydrogen bonding network in $\text{Te}(\text{OH})_6$, it was decided to carry out a neutron diffraction study.

EXPERIMENTAL

Crystal growth. The crystal used for the neutron diffraction work was obtained from a saturated solution sealed in a cell at room temperature to prevent too rapid evaporation. The temperature of the solution was gradually lowered by a total amount of 5°C over a period of 20 h in order to obtain supersaturation. After a week at the lower temperature, a single crystal of suitable size for neutron diffraction measurements had formed. The crystal, which showed some well-developed faces, while others were more irregular in shape (cf. Fig. 1), had a maximum linear dimension of 7 mm.

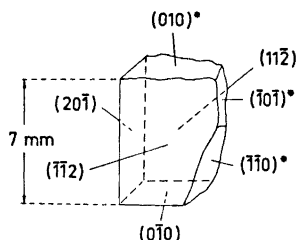


Fig. 1. The morphology of the crystal used for data collection.

Data collection. The intensity measurements were carried out on a Hilger-Ferranti automatic four circle diffractometer located at the Danish Atomic Energy Research Establishment, Risø. The moving crystal and fixed detector technique (ω scan) was used in the measurements with a neutron wave length of 1.025 Å. The monochromatic neutron beam was uniform within $\pm 3\%$ for the area ranging over the crystal.

The crystal was mounted with the b axis along the ϕ axis of the instrument. In measuring the reflections the crystal was rotated $\pm 3^\circ$ alternately about the diffraction vector from the A-setting position, thereby at least avoiding simultaneous reflection from $0k0$ and $h0l$, when hkl was recorded.

A total of 1440 reflections with $k \geq 0$ and $\sin \theta/\lambda < 0.55 \text{ \AA}^{-1}$ were measured in increasing order of $\sin \theta/\lambda$. A standard reflection, $\bar{1}12$, was measured at intervals of 15. Step scan measurements were used, and counts for each step were recorded. The total scan interval was 4° , and the size of the step was 0.08° . The space group is $P2_1/n$, and the space group extinctions $0k0$ for k odd, and $h0l$ for $h+l$ odd were included in the reflections measured.

Data reduction. The unit cell determined by the X-ray work,¹ *i.e.* $a = 6.495$, $b = 9.320$, $c = 11.393 \text{ \AA}$ and $\beta = 133.88^\circ$, was used.

The reflection profiles were reduced to structure factors using a method which determines the points of division between the peak and the background so that $\sigma(I)/I$ is minimized,² where I is the integrated intensity and $\sigma(I)$ its standard deviation based on counting statistics.

The reflections were corrected for drift in the experimental conditions as reflected by the variation of the intensity of the standard reflection. This variation was of the order of 2% within the measuring period.

An absorption correction was performed using the program DATAPH.³ The calculated linear absorption coefficient is $\mu = 1.90 \text{ cm}^{-1}$, assuming the incoherent scattering cross-section of the hydrogen atom to be 38 b. The poorly developed faces of the crystal were approximated to crystallographic planes as shown in Fig. 1, the distances to the boundary planes from an internal origin being given in Table 1. The distances to the planes

Table 1. Crystal dimension. The distances from an internal origin to the boundary planes are given. Those planes marked with an asterisk are approximations (*cf.* Fig. 1).

Plane	d (mm)
(010)*	2.7
(0 $\bar{1}$ 0)	2.7
(11 $\bar{2}$)	1.0
($\bar{1}$ 12)	1.0
(20 $\bar{1}$)	1.7
(101)*	1.8
($\bar{1}$ 10)*	1.2
Crystal volume = 40.3 mm ³	

$(\bar{1}0\bar{1})^*$ and $(\bar{1}\bar{1}0)^*$ were obtained after small adjustments giving an absorption correction which accounted for the intensity variation of the 020 reflection as a function of ϕ . The crystal was divided into $6 \times 8 \times 4$ Gaussian points along the a , b , and c directions, respectively. The calculated transmission factors varied between 0.52 and 0.68.

The symmetry related reflections were averaged, and 591 reflections having $F^2 > 4\sigma(F^2)$ were used for the refinement of the structure.

REFINEMENT OF THE STRUCTURE

The positions of the hydrogen atoms were determined from a nuclear density summation, starting from the tellurium and oxygen parameters obtained in the X-ray work.¹ Minima corresponding to all hydrogen atoms in the cell were clearly resolved.

The refinement of the structure was performed with the least squares program LINUS,⁴ and the neutron scattering lengths for the different atoms were $b_{\text{H}} = -3.72$ F, $b_{\text{Te}} = 5.6$ F (The Neutron Diffraction Commission⁵) and $b_{\text{O}} = 5.88$ F (Brown and Chidambaram⁶). The quantity minimized was $\sum w ||F_{\text{o}}| - |F_{\text{c}}||^2$.

The weights initially used were based on the standard deviations of the structure factors modified as $\sigma_{\text{mod}} = (\sigma(F^2) + 1.025F^2)^{\frac{1}{2}} - |F|$. Since this procedure tended to overweight the weak reflections, an artificial weighting

$$w^{-\frac{1}{2}} = \sigma_{\text{art}} = \begin{cases} [c - (F - a)^{\frac{1}{2}}]^{\frac{1}{2}}, & F > a \\ (c \times a/F)^{\frac{1}{2}}, & F \leq a \end{cases}$$

scheme was used. When $a = 20.6$ and $c = 33.3$ a more reasonable weighting was obtained (cf. Table 2).

Table 2. Agreement analyses using weights based on (a) σ_{mod} and (b) σ_{art} . $R = \sum |F_{\text{o}} - |F_{\text{c}}|| / \sum F_{\text{o}}$, $R_w = (\sum w |F_{\text{o}} - |F_{\text{c}}||^2 / \sum w F_{\text{o}}^2)^{\frac{1}{2}}$ and $w\Delta^2$ are normalized quantities $\sum w |F_{\text{o}} - |F_{\text{c}}||^2 / N$, where N is the number of reflections in the relevant F_{o} interval.

F_{o} interval	N	(a) $w\Delta^2$	(b) $w\Delta^2$
0.0 - 6.8	45	2.85	1.97
6.8 - 9.3	63	2.45	1.78
9.3 - 12.2	64	1.12	0.90
12.2 - 16.1	66	0.71	0.55
16.1 - 20.7	74	0.66	0.60
20.7 - 25.3	68	0.38	0.39
25.3 - 30.6	44	0.56	0.54
30.6 - 42.5	72	0.71	1.41
42.5 - 59.4	52	0.54	1.13
59.4 - 110.0	43	0.25	0.95
		$R = 0.025$	$R = 0.024$
		$R_w = 0.033$	$R_w = 0.019$

Although the weak reflections were given low weight in the refinement, the $w\Delta^2$ values are highest for these data, as is seen in Table 2. The F_{c} values are often too small, which, in some cases may be due to multiple reflection

effects, or merely a result of the fact that, among the reflections just above the limit of acceptance, the statistical counting errors do not conform to the normal distribution curve.

The final atomic parameters are given in Table 3 and observed and calculated structure factors are compared in Table 4.

Table 3. Final neutron diffraction parameters in $\text{Te}(\text{OH})_6$. The anisotropic temperature factor is $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + hka^*b^*U_{12} + hla^*c^*U_{13} + klb^*c^*U_{23})]$. The numbers in parentheses are the e.s.d.'s calculated by the least squares program.

Atom	x	y	z
Te_1	0	0	0
Te_2	0	0	$\frac{1}{2}$
O_1	0.7324(2)	0.1543(2)	0.8943(2)
O_2	0.1252(3)	0.0486(1)	0.2038(2)
O_3	0.7741(3)	0.3751(2)	0.5378(2)
O_4	0.6921(2)	0.0968(2)	0.4545(2)
O_5	0.3251(3)	0.4511(1)	0.7850(2)
O_6	0.7193(3)	0.3270(1)	0.0789(2)
H_1	0.2397(5)	0.2864(3)	0.4688(3)
H_2	0.3306(6)	0.0695(3)	0.2913(3)
H_3	0.4720(6)	0.0931(3)	0.1246(3)
H_4	0.7337(5)	0.1989(3)	0.4873(3)
H_5	0.9476(5)	0.0359(3)	0.2638(3)
H_6	0.8983(6)	0.3332(3)	0.1941(3)

	$U_{11} \times 10^4$	$U_{22} \times 10^4$	$U_{33} \times 10^4$	$U_{12} \times 10^4$	$U_{13} \times 10^4$	$U_{23} \times 10^4$
Te_1	62(10)	119(10)	74(10)	34(10)	74(17)	28(13)
Te_2	85(10)	105(10)	98(11)	-18(12)	124(17)	3(13)
O_1	128(6)	163(7)	135(7)	86(10)	114(11)	16(12)
O_2	109(9)	324(9)	105(7)	-16(17)	131(15)	-89(11)
O_3	105(8)	191(7)	225(7)	35(11)	170(14)	-120(11)
O_4	117(7)	191(10)	194(7)	-13(10)	200(14)	-80(12)
O_5	104(7)	322(8)	118(7)	-34(10)	140(12)	-91(11)
O_6	141(8)	146(6)	145(9)	92(10)	133(16)	1(11)
H_1	285(12)	258(13)	271(13)	-117(19)	363(22)	30(23)
H_2	212(17)	442(14)	199(12)	-57(22)	226(18)	-152(22)
H_3	153(16)	359(14)	274(13)	8(21)	237(26)	110(22)
H_4	273(12)	236(17)	346(13)	4(21)	405(22)	-124(23)
H_5	262(13)	442(15)	222(12)	35(21)	389(22)	40(20)
H_6	225(14)	278(13)	214(16)	83(19)	177(28)	46(19)

In addition to atomic coordinates and anisotropic thermal vibration parameters, an isotropic secondary extinction parameter and the scattering length of tellurium were allowed to vary in the refinement. The extinction effect was unusually small, resulting in a maximum correction to the intensities of less than 3 %.

The tellurium scattering length was refined since the tabulated values are of low precision. Starting from $b_{\text{Te}} = 5.6 \text{ F}^6$ for both Te atoms, the b values of Te_1 and Te_2 were refined independently, giving $b_{\text{Te}_1} = 5.79 \pm 0.06 \text{ F}$ and

Table 4. Continued.

1 1 6	237	-273	1 4 -6	89	65	1 6 -2	217	221	1 9 1	0	-8	0 4 -4	96	68	
1 1 7	203	-177	1 4 -7	133	-147	1 6 -1	0	39	1 9 2	562	561	0 4 -3	285	-291	
1 1 7	-9	0	29	1 4 -6	136	131	1 6 0	717	218	1 10 -2	124	131	0 4 -2	412	-419
1 2 -8	0	-13	1 4 -9	128	134	1 6 1	443	-441	1 10 -1	67	-37	0 4 -1	191	-233	
1 2 -7	71	-29	1 4 -4	383	-391	1 6 2	179	176	1 10 0	219	219	0 4 0	293	-286	
1 2 -6	98	98	1 4 -3	147	-160	1 6 3	59	70	0 0 -8	223	-231	0 5 -7	144	146	
1 2 -5	114	136	1 4 -2	386	-387	1 6 4	135	-115	0 0 -6	228	-429	0 5 -6	0	32	
1 2 -4	245	245	1 4 -1	167	-131	1 7 -7	185	-179	0 0 -4	91	84	0 5 -5	0	38	
1 2 -3	0	-1	1 4 3	475	-473	1 7 -6	91	37	0 0 -2	514	510	0 5 -4	367	375	
1 2 -2	95	94	1 4 1	67	44	1 7 -5	244	244	0 1 -8	163	-162	0 5 -3	95	-84	
1 2 -1	0	22	1 4 2	296	-296	1 7 -4	682	685	0 1 -7	90	-80	0 5 -2	143	-150	
1 2 0	69	-47	1 4 3	70	68	1 7 -3	495	-422	0 1 -6	351	-362	0 5 -1	68	62	
1 2 1	250	247	1 4 4	235	-241	1 7 -2	444	450	0 1 -5	324	330	0 6 -7	151	149	
1 2 2	675	631	1 4 5	117	117	1 7 -1	637	-658	0 1 -4	282	-279	0 6 -6	179	-179	
1 2 3	291	-294	1 4 6	0	28	1 7 0	0	22	0 1 -3	187	-185	0 6 -5	259	265	
1 2 4	160	167	1 4 7	112	-133	1 7 1	344	-536	0 1 -2	66	52	0 6 -4	236	-244	
1 2 5	0	16	1 4 8	369	-363	1 7 2	114	112	0 2 -8	0	12	0 6 -3	223	228	
1 2 6	88	84	1 5 -7	564	-568	1 7 3	643	-447	0 2 -7	773	-777	0 6 -2	298	359	
1 2 7	99	-86	1 5 -6	273	-273	1 7 4	243	-242	0 2 -6	586	501	0 6 -1	184	-168	
1 3 -9	225	213	1 5 -5	0	-7	1 7 5	339	426	0 2 -5	350	-361	0 6 0	366	368	
1 3 -8	236	238	1 5 -4	148	155	1 8 -6	236	-229	0 2 -4	638	648	0 7 -6	57	-66	
1 3 -7	345	-349	1 5 -3	179	-213	1 8 -5	750	247	0 2 -3	248	252	0 7 -5	156	-152	
1 3 -6	542	543	1 5 -2	236	242	1 8 -4	177	162	0 2 -2	259	254	0 7 -4	213	-211	
1 3 -5	615	617	1 5 -1	59	45	1 8 -3	147	148	0 2 -1	0	-8	0 7 -3	82	78	
1 3 -4	418	-415	1 5 0	279	232	1 8 -2	0	25	0 2 0	578	512	0 7 -2	167	-174	
1 3 -3	92	166	1 5 1	576	571	1 8 -1	175	169	0 3 -8	127	136	0 7 -1	343	351	
1 3 -2	0	-19	1 5 2	472	466	1 8 0	65	-46	0 3 -7	195	-195	0 8 -5	268	264	
1 3 -1	123	133	1 5 3	399	-471	1 8 1	136	-141	0 3 -6	110	-118	0 8 -4	352	359	
1 3 0	167	168	1 5 4	457	423	1 8 2	0	79	0 3 -5	109	-93	0 8 -3	506	508	
1 3 1	621	626	1 5 5	0	-27	1 8 3	196	-254	0 3 -4	352	361	0 8 -2	486	485	
1 3 2	520	526	1 5 6	617	609	1 8 4	82	-83	0 3 -3	0	18	0 8 -1	0	-45	
1 3 3	76	-97	1 6 -8	136	120	1 9 -9	93	87	0 3 -2	202	206	0 8 0	312	312	
1 3 4	858	825	1 6 -7	73	78	1 9 -8	175	114	0 3 -1	155	-166	0 9 -4	69	-91	
1 3 5	281	298	1 6 -6	15	-95	1 9 -3	63	51	0 4 -8	215	219	0 9 -3	261	257	
1 3 6	58	-49	1 6 -5	135	135	1 9 -2	0	0	0 4 -7	0	8	0 9 -2	0	6	
1 3 7	373	-383	1 6 -4	0	23	1 9 -1	85	74	0 4 -6	372	372	0 9 -1	91	-95	
1 4 -9	56	-47	1 6 -3	161	154	1 9 0	61	-52	0 4 -5	245	-242	0 10 -1	133	-126	
												0 10 0	178	-183	

$b_{\text{Te}_2} = 5.81 \pm 0.06$ F. The resulting value, $b_{\text{Te}} = 5.80$ F, is probably more reliable than the lower value determined previously, since it is based on the more accurately known scattering lengths of hydrogen⁵ and oxygen.⁶

DISCUSSION

The Te-O₆ octahedra. The higher precision of the neutron diffraction data has enabled the molecular dimensions of $\text{Te}(\text{OH})_6$ to be determined with appreciably better precision than was obtained in the previous X-ray investigation. However, the improvement in the Te-O bond determination can also be ascribed to the fact that the Te-O distances are determined solely by the oxygen positions, since all tellurium parameters are fixed by the symmetry.

Table 5. Distances and angles within the two tellurium-oxygen coordination polyhedra. The angles listed are those indicated in Fig. 4, where Te_1 corresponds to the tellurium atom at the origin in Fig. 3. E.s.d.'s are given in parentheses. No distances have been corrected for thermal motion.

Distances		Angles	
Te_1-O_1	1.907(1) Å	$\text{O}_1-\text{Te}_1-\text{O}_2$	88.69(7)°
Te_1-O_2	1.908(1)	$\text{O}_1-\text{Te}_1-\text{O}_3$	91.07(6)
Te_1-O_3	1.910(1)	$\text{O}_2-\text{Te}_1-\text{O}_3$	92.08(7)
Te_2-O_4	1.908(1)	$\text{O}_4-\text{Te}_2-\text{O}_5$	87.60(6)
Te_2-O_5	1.908(1)	$\text{O}_4-\text{Te}_2-\text{O}_6$	88.38(6)
Te_2-O_6	1.914(1)	$\text{O}_5-\text{Te}_2-\text{O}_6$	90.71(7)

The tellurium–oxygen bond distances and angles are given in Table 5, and stereoscopic drawings, obtained with the program ORTEP,⁷ are shown in Figs. 2 and 3.

The average Te–O bond distance of 1.909 ± 0.001 Å is in good agreement with the X-ray value of 1.916 ± 0.005 Å. In both the neutron and X-ray investigations, it has been found that the $\text{Te}_2\text{–O}_6$ bond is slightly longer than

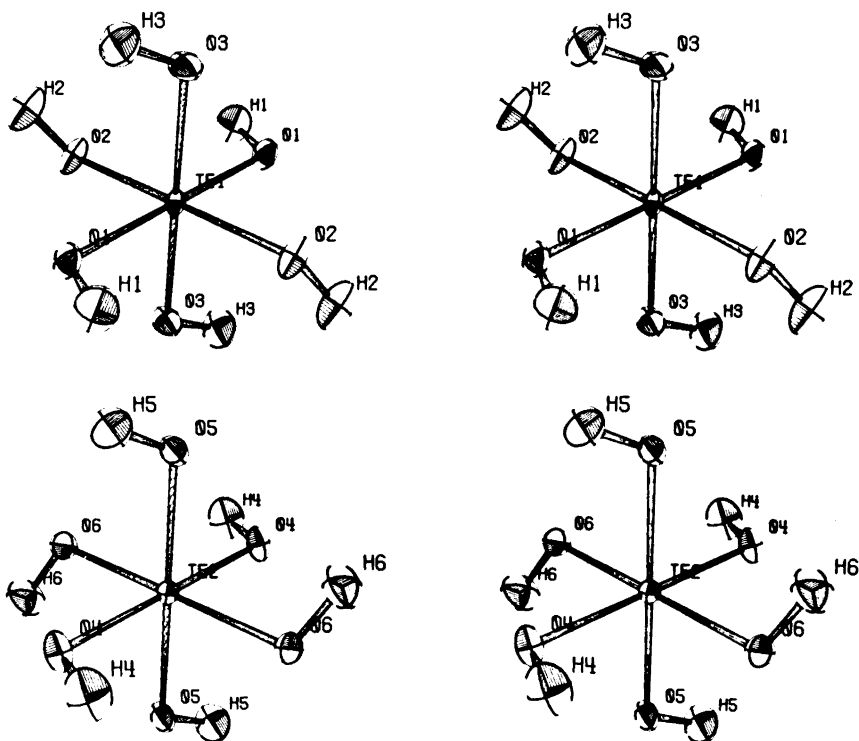


Fig. 2. Stereoscopic pictures⁷ of the two independent $\text{Te}(\text{OH})_6$ molecules. The thermal ellipsoids enclose areas with an atomic probability density greater than 50 %.

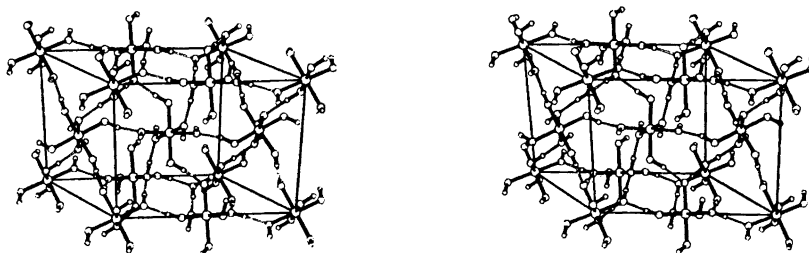


Fig. 3. Stereoscopic picture⁷ showing all atoms bonded to tellurium atoms within one unit cell. The cell is viewed along the a^* direction.

the other Te–O bonds, and, according to the neutron diffraction results, this bond may be significantly longer than the Te₂–O₄ and Te₂–O₅ bonds. There seems to be no obvious reason for this effect, but it is possible that the hydrogen bonds in the structure may cause deviations from the ideally octahedral oxygen coordination around tellurium. That this is the case is clearly indicated in the significant deviations of the O–Te–O angles from 90°, as discussed below.

A comparison of the Te–O coordination in Te(OH)₆ with that in other tellurates was given in the previous paper.¹

Hydrogen bonds. The hydrogen positions determined in the X-ray investigation have been shown to be reasonable, and thus the hydrogen bonding network indicated in Fig. 2 and Table 8 of Ref. 1 is correct. However, no detailed discussion of the hydrogen bonds was possible at that stage, since the e.s.d.'s of the hydrogen positions were as high as 0.1 Å. The neutron diffraction results are given in Table 6.

Table 6. Hydrogen bonding in telluric acid.

	O–O	O–H	H...O	∠O–H...O	∠Te–O–H	∠H...O–Te
Te ₁ –O ₁ –H ₁ ...O ₆ –Te ₂	2.695(2) Å	0.989(3) Å	1.711(3) Å	173.4(3)°	113.6(2)°	129.7(1)°
Te ₁ –O ₂ –H ₂ ...O ₄ –Te ₂	2.709(2)	0.983(3)	1.727(3)	175.3(3)	114.5(2)	129.4(1)
Te ₁ –O ₃ –H ₃ ...O ₅ –Te ₂	2.696(2)	0.977(3)	1.720(3)	175.8(3)	114.2(2)	127.8(1)
Te ₂ –O ₄ –H ₄ ...O ₃ –Te ₁	2.685(2)	0.990(3)	1.698(3)	174.5(2)	113.1(2)	127.6(1)
Te ₂ –O ₅ –H ₅ ...O ₂ –Te ₁	2.676(2)	0.987(3)	1.704(3)	167.2(3)	115.0(2)	126.2(1)
Te ₂ –O ₆ –H ₆ ...O ₁ –Te ₁	2.730(2)	0.983(3)	1.750(3)	175.1(3)	112.6(2)	127.0(1)
		∠H ₆ ...O ₁ –H ₁		∠H ₂ ...O ₄ –H ₄	111.1(2)	
		∠H ₅ ...O ₂ –H ₂		∠H ₃ ...O ₅ –H ₅	118.4(2)	
		∠H ₄ ...O ₃ –H ₃		∠H ₁ ...O ₆ –H ₆	113.3(2)	

The O–H...O distances, ranging from 2.676 Å to 2.730 Å with a mean value of 2.699 Å, indicate rather strong hydrogen bonding in the structure. The complex three-dimensional hydrogen bond network is of (12,8) type (*cf.* the monograph by Hamilton and Ibers,⁸ p. 21), *i.e.* each molecule is involved in twelve hydrogen bonds to eight neighbouring molecules (*cf.* Fig. 3). Six of these bonds are directed octahedrally towards six other molecules, a three-dimensional network thus being formed. The remaining six all extend approximately along the [102] direction, making three connections to each of the two adjacent molecules, thus in this direction resulting in the formation of chains running through the structure (*cf.* Fig. 4).

There is no hydrogen bonding between symmetry related Te(OH)₆ molecules. The main difference between the two independent molecules in the cell is that the Te₁ molecule supplies four hydrogen atoms to the chain bonds and only two to the octahedral bonds, while these numbers are reversed for Te₂ (*cf.* Fig. 3).

None of the O–H bonds are significantly different from the average value 0.985 Å, but there are small differences among the H...O bonds. Hamilton and Ibers⁸ have investigated the correlation between the O–H

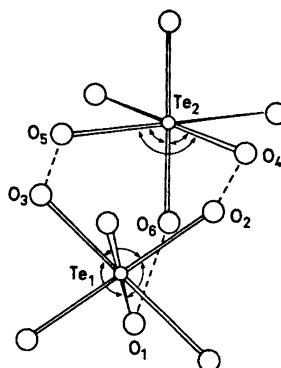


Fig. 4. Schematic drawing indicating the angles listed in Table 5. The unmarked angles are given from symmetry (Te_1 and Te_2 at $\bar{1}$).

bond length and the O—H...O and H...O distances, respectively. In the present investigation, the average H...O bond distance is 1.718 Å, and, according to the empirical curve given by Hamilton and Ibers, this value should correspond to an O—H bond length of 0.99 Å. This is in good agreement with the value of 0.985 Å actually found in $\text{Te}(\text{OH})_6$.

The O—H...O angles are close to 175° (except for angle $\text{O}_5\text{—H}_5\cdots\text{O}_2$ which is 167.2°) and they are slightly smaller than in the other pure hydroxy-acid known, orthoboric acid. In a neutron diffraction study of D_3BO_3 these angles were found to range from 175.5° to 179.4°.⁹ In both compounds, the hydrogen atom is closer to the centre of the molecule than it would have been if the hydrogen bonds had been linear (exception: D_4 in D_3BO_3). In the similar compound H_5IO_6 ,¹⁰ the range 171—178° has been found.

The Me—O—H and H...O—Me angles are of the same magnitudes in D_3BO_3 , H_5IO_6 , and $\text{Te}(\text{OH})_6$, whereas the average H...O—H angle in $\text{Te}(\text{OH})_6$ is 114.0° compared to 119.8° for $\text{D}\cdots\text{O—D}$ in D_3BO_3 . In orthoboric acid, the arrangements of atoms around the oxygen atoms is approximately planar, while in telluric acid the oxygen atom is significantly tilted out of the corresponding plane permitting a smaller O...H—O angle. An assumption of sp^2 hybridization of the oxygen atoms and double $\sigma\pi$ Te—O bonds (according to the Te—O bond length) seems reasonable as a first approximation. However, it is difficult to quantitatively discuss the deviations from 120° of the angles subtended at the oxygen atoms.

In a recent powder neutron diffraction investigation of cubic telluric acid the hydrogen atoms were found to be statistically distributed.¹¹ A detailed comparison of the hydrogen bonds in the two modifications is therefore not possible. It would appear that the more stable monoclinic phase, with its localized hydrogen positions, can be described as being slightly distorted from cubic symmetry.

When hydrogen bonds are formed changes occur in the parts of the molecules involved. In telluric acid the molecules are connected solely through hydrogen bonds and all hydrogen atoms participate, moreover, in similar hydrogen bonds. It ought therefore to be possible to see what influence the hydrogen bonds have on the tellurium coordination and thus obtain some

indications as to how they arise. Assuming that in a free $\text{Te}(\text{OH})_6$ molecule the oxygen atoms form a regular octahedron around Te, the main distortion caused by the hydrogen bonding in the $\text{Te}(\text{OH})_6$ crystal is that the $\text{O}-\text{Te}-\text{O}$ angles are no longer 90° . One might expect to find decreased angles as a result of the $\text{O}-\text{H}\cdots\text{O}$ attractions where two molecules are connected over three hydrogen bonds (*cf.* Fig. 4). This is not, however, the case. Nor is it possible to explain the deviations in terms of strains caused by the preference of any particular $\text{Te}-\text{O}-\text{H}$ angle. There is, moreover, no correlation between hydrogen to hydrogen repulsion and the $\text{O}-\text{Te}-\text{O}$ angles (*cf.* Fig. 5). The

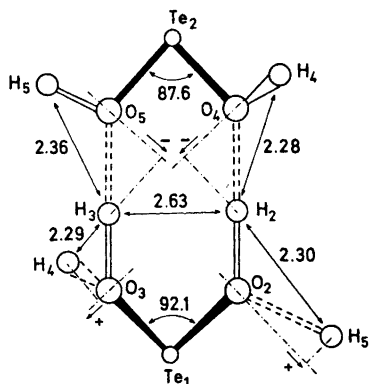


Fig. 5. Schematic drawing showing the effect of the hydrogen bonds on the $\text{O}-\text{Te}-\text{O}$ angles.

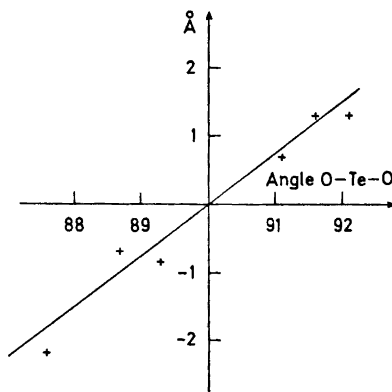


Fig. 6. Correlation between acceptor directions in the hydrogen bonds and the deviations of the $\text{O}-\text{Te}-\text{O}$ angles from 90° . For each angle, the sum of the two $\text{H}\cdots\text{O}$ projections (*cf.* Fig. 5) has been plotted.

deviations of the oxygen atoms from their ideal octahedral positions might, however, be attributable to their role as acceptors in the hydrogen bonds. In order to examine this effect more quantitatively, the acceptor bonds $\text{O}_a\cdots\text{H}$ and $\text{O}_b\cdots\text{H}$ were projected on lines in the plane of the $\text{O}_a-\text{Te}-\text{O}_b$ angle under consideration. These lines were perpendicular to the $\text{Te}-\text{O}_a$ and $\text{Te}-\text{O}_b$ bonds, respectively, and their positive directions were defined as indicated in Fig. 5. From Fig. 6, in which the sum of the two $\text{O}_a\cdots\text{H}$ and $\text{O}_b\cdots\text{H}$ projections for each of the six independent $\text{O}_a-\text{Te}-\text{O}_b$ angles has been plotted against the value of the angle, it is evident that there is a correlation, indicated by a straight line through the origin. The method of just adding the two components for each angle may be crude, and some of the effects mentioned above might also affect the positions of the points in the diagram. The rotation of the $\text{O}-\text{H}$ bond around the $\text{Te}-\text{O}$ bond, necessary for the formation of the hydrogen bond network, might also disturb the $\text{Te}-\text{O}$ $\sigma\pi$ bonding system.

The correlation between the direction of the lone pair of the acceptor oxygen atoms, which is presumably near the hydrogen bond direction, and

the O—Te—O angles (*cf.* Fig. 6) indicates that the increased electron density in the direction towards the H—O donor is large enough to cause the acceptor oxygen nucleus to shift its equilibrium position in this direction. Thus, when hydrogen bonds are formed in $\text{Te}(\text{OH})_6$, the main change in the system seems to be concentrated in the accepting lone pair.

As discussed above, the donor O—H bond length is increased by formation of hydrogen bond. In $\text{Te}(\text{OH})_6$, this lengthening may partly be regarded as a result of a decreased electron density in the O—H bond caused by transfer of electron density towards the oxygen lone pair directed towards a hydrogen atom in a neighbouring molecule.

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