Acta Cryst. (1966). **21**, 578

The Crystal Structure of Basic Tellurium Nitrate, $Te_2O_4.HNO_3$

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(*Received* 24 *January* 1966)

The structure of $Te_2O_4.HNO_3$ (the product of dissolving Te or TeO_2 in HNO_3) has been determined from visual intensities collected with Mo $K\alpha$ radiation, and refined to $R=7\%$. The crystals are orthorhombic, *Pnma*, with 4 formula units in a unit cell of dimensions $a=14{\cdot}55$, $b=8{\cdot}77$, $c=4{\cdot}45$ Å. The structure consists of puckered layers of tellurium and oxygen atoms. Each tellurium atom is linked to one other by two oxygen bridges and to two others by a single oxygen bridge each. The four tellurium–oxygen bonds around a tellurium atom are directed approximately toward the axial and two equatorial apices of a trigonal bipyramid. The tellurium–oxygen bond lengths range from 1·88 to 2·16 Å, with an average estimated standard deviation of 0·015 Å. The nitrate group is hydrogen-bonded to one of the bridging oxygen atoms, with $O\cdots O=2{\cdot}75$ Å.

Introduction

Although tellurium exhibits a variety of coordination patterns, accurate crystal structure details are rare even for its simple compounds. For instance, the two crystallographic forms of TeO_2 have been studied in some detail: tellurite (orthorhombic β-TeO_2) has been classified as a distorted brookite-type structure (Ito & Sawada, 1939); tetragonal α-TeO_2 gave fair agreement as a direct analogue of rutile (Goldschmidt, 1926), but more recent studies (Stehlik & Balak, 1949; Leciejewicz, 1961) show that it is a distorted variant of the rutile structure. Except for values in the last of these references, realistically estimated standard deviations for tellurium–oxygen bond lengths are greater than 0·1 Å. The structure of 'basic tellurium nitrate', $Te_2O_4.HNO_3$, was selected for study not only to determine the nature of this particular compound, but also to provide more information about coordination patterns around tellurium and about tellurium-oxygen bond lengths.

Experimental

A preliminary investigation of this material (Heiart, 1956) yielded the following crystallographic data:

Orthorhombic		$a=14{\cdot}547\ (0{\cdot}042)$ Å
$\varrho_{\text{obs}}=4{\cdot}36$ g.cm^{-3}		$b=8{\cdot}770\ (0{\cdot}006)$
$\varrho_{\text{calc}}=4{\cdot}48$ g.cm^{-3}	for $Z=4$	$c=4{\cdot}446\ (0{\cdot}004)$

where values in parentheses are estimated standard deviations. Systematic absences indicate that the space group is *Pnma* or $Pn2_1a$.

Basic tellurium nitrate was readily prepared by dissolving metallic tellurium in nitric acid, followed by several recrystallizations. A small single crystal was selected and used to obtain precession *h0l*, *h1l*, *0kl*, *1kl* data, then Weissenberg *hkl* data for $l=0$ through 6 with the usual multiple film technique; Mo $K\alpha$ radiation was used to reduce absorption further. Intensities were estimated visually on the basis of a series of standard intensity scales. Lorentz-polarization corrections were estimated graphically for the precession data and the Zalkin–Templeton Incor program was used to correct the Weissenberg data.

For further experimental evidence relating to hydrogen bonding, infrared spectra were obtained by both KBr pellet and Nujol mull techniques. The instrument used was a Perkin–Elmer 21 and the pellet spectrum was calibrated against that of polystyrene.

Structure determination

In view of the short *c* axis and the presence of a heavy atom, it was originally expected that the structure could be solved in projection. A Patterson projection down the short *c* axis located the tellurium atoms (Heiart, 1956). This same projection, $P(u,v)$, showed a row of prominent peaks on the line $P(0,v)$ which strongly suggested atoms related by (010) mirror planes and thus indicated *Pnma* as the probable space group rather than $Pn2_1a$. The projection did not lead to the complete structure because what seemed to be too many peaks were found in the electron density calculated with signs determined by the tellurium atom (the correct structure contains only two independent oxygen atoms in eightfold general positions and three independent oxygen atoms in fourfold special positions instead of four and one, as originally guessed).

Subsequent work used three-dimensional calculations. The *z* coordinate of the tellurium atom was estimated to be near zero from the generally small intensities of reflections depending on the factor $\sin 2\pi lz$, and in fact to be roughly 0·02 from the slightly faster-than-normal decline with increasing *l* for reflections depending on the factor $\cos 2\pi lz$.

Signs were alloted to all reflections according to the tellurium contribution, and the three-dimensional difference density was calculated with tellurium contri-

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butions subtracted. The difference map indicated considerable anisotropy in the thermal motion of all atoms and was especially rough in the tellurium neighborhood. Nevertheless, the correct number of peaks were found in structurally reasonable positions and starting parameters were assigned to all atoms except the hydrogen atom.

Refinement was continued using the BXLS block diagonal least-squares program (Carpenter, 1963) minimizing the quantity

$$R_w = [\Sigma\, w(\Delta F)^2 / \Sigma\, w|F|_o^2]^{\frac{1}{2}}$$

with a single scale factor for all data. The weights, w, were assigned according to the formulas:

$$w = \sigma^{-2}, \quad \sigma \simeq 2{\cdot}3 + 0{\cdot}08 N^{-\frac{1}{2}} |F|_o + 0{\cdot}005 |F|_o^2 ,$$

N being the number of independent observations for a particular structure factor. The coefficients, originally estimated from the internal consistency of the data, are expressed above on the same scale as the values of $|F|_o$ in Table 2. Reflections too weak for accurate measurement were given zero weight.

Five cycles of isotropic refinement reduced the discrepancy indices from $R=0{\cdot}178$ and $R_w=0{\cdot}263$ to $R=0{\cdot}114$ and $R_w=0{\cdot}157$ for observed reflections only. After the fifth cycle, a difference map indicated that the prominent remaining discrepancy was due to anisotropic thermal motion.

Because of the overwhelming contribution from tellurium to most of the structure factors, it was expected, and later confirmed, that anisotropic thermal parameters for the light atoms would not refine properly. Several cycles of partial anisotropic refinement were carried out by manually shifting to equivalent isotropic parameters for the lighter atoms after each cycle. This refinement procedure converged to a structure with $R=0{\cdot}088$, $R_w=0{\cdot}114$.

Since the difference map was still rather rough near the tellurium atom, further refinements were necessary. Before proceeding, extinction corrections were applied to reflections corresponding to the 25 strongest observed intensities using the approximation

$$F_{\text{corr}} = F_{\text{obs}}(1 + cJ_{\text{obs}})$$

(Zachariasen, 1963) and the recent HFS scattering factor (Hanson, Herman, Lea & Skillman, 1964) for tellurium was corrected for the real part of the anomalous dispersion (Cromer, 1965) for use in subsequent refinement. Lorentz-polarization corrections and interlayer scale factors had been applied to the original data by hand and a reflection-by-reflection check of the data uncovered a number of errors. The effect of extinction on the $hk0$ reflections and a systematic error in Lp corrections for $hk6$ data required that the observed structure factors for these layers be scaled down by 5%.

Concurrently, the BXLS program was modified to allow refinement of some atoms while including others only for their contribution to the structure factors. This made it possible to run alternate cycles, refining the tellurium anisotropically while holding the lighter atoms fixed, then refining the light atoms isotropically while holding the tellurium parameters constant.

Refinement was continued until all coordinate shifts were < 10% of their calculated standard deviations. Final discrepancy indices for the 426 observed reflections only were $R=0{\cdot}069$ and $R_w=0{\cdot}092$ with final atomic coordinates of Table 1. Table 2 lists the observed and calculated structure factors based on the final parameters given in Table 1.

The final difference function was within the range of expected fluctuations except for two peaks associated with a periodic disturbance (period $c/6$) extending in the c direction from the tellurium atom. The largest such peak had a height of 4 e.Å^{-3} ($2{\cdot}8\sigma$), less than half the height of the smallest oxygen peak in the first difference map.

Discussion of the structure

The overall packing plan for basic tellurium nitrate is a series of puckered tellurium–oxygen networks extended in two dimensions normal to the a axis. The nitrate groups are connected to this framework by

Table 1. *Final atomic parameters*

Estimated standard deviations are in parentheses*

	x/a	y/b	z/c	B
Te(1)	0·16655 (10)	0·06355 (17)	0·02001 (24)	†
O(2)	0·2106 (11)	0·0279 (19)	0·4110 (36)	0·98 (21) Å^2
O(3)	0·2334 (16)	$\frac{1}{4}$	0·9234 (52)	1·00 (33)
O(4)	0·0917 (20)	$\frac{1}{4}$	0·2241 (66)	1·88 (46)
N(5)	0·4386 (23)	$\frac{1}{4}$	0·7105 (70)	1·65 (48)
O(6)	0·3787 (18)	$\frac{1}{4}$	0·5267 (61)	1·52 (38)
O(7)	0·4662 (16)	0·1260 (26)	0·8260 (53)	2·37 (37)

Te(1) $\beta_{11}=0{\cdot}00152$ (4) $\beta_{22}=0{\cdot}00271$ (11) $\beta_{33}=0{\cdot}00462$ (32)
$\beta_{12}=0{\cdot}00013$ (21) $\beta_{23}=0{\cdot}00008$ (65) $\beta_{31}=0{\cdot}00030$ (39)

for a temperature factor of the form

$$\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{23}kl+\beta_{31}lh)]$$

* Thermal parameters from a block diagonal refinement and standard deviations from a diagonal approximation, as given in this table, are less meaningful than those given by a full matrix refinement.

† Equivalent isotropic parameter (for comparison) $\hat{B}_{\text{Te}}=0{\cdot}83$.

hydrogen bonds and all distances between atoms in adjacent layers are larger than the normal van der Waals distances. Therefore, details of the arrangement of atoms within one of these layers is of primary interest.

Fig. 1 shows a section of this network projected along the *a* axis. The principal interatomic distances and angles are listed in Table 3. Fig. 2 is a *b*-axis projection of the section between adjacent mirror planes. A stereoscopic drawing, Fig. 3, is included for those who have stereo viewers or flexible eyes.

The curious tellurium–oxygen bonding pattern can be thought of as the skeleton of the structure. Distorted double oxygen bridges join tellurium atoms across the mirror planes and single oxygen bridges between tellurium atoms link these Te_2O_2 units into a network normal to the *a* axis. Around any one tellurium atom there are four short tellurium–oxygen distances between 1·88 and 2·16 Å, and three longer distances between 2·8 and 2·9 Å. The difference between any two of the four shortest distances is definitely significant (confidence level ≥0·999, based on the BXLS formal estimated standard deviations). The shortest tellurium–tellurium distance is 3·27 Å across the mirror plane, and sucessive tellurium atoms in the –Te–O–Te– chain are 3·48 Å apart.

Since the tellurium–oxygen bonding in $Te_2O_4.HNO_3$ may be expected to be closely related to that in tellurite (β-TeO_2) and tetragonal α-TeO_2, the results reported for these compounds were examined in detail. The data for tellurite (Ito & Sawada, 1939), were found to be inadequate for extraction of sufficiently precise structural detail (we plan further work on tellurite).* In the most recent report on the structure of α-TeO_2 (Leciejewicz, 1961) several errors (interatomic distances, angles, *etc.*) were found although the atomic coordinates seem to be correct. Allowing for these discrepancies, a similar arrangement for the four nearest neighbor oxygen atoms about the tellurium

Table 2. *Observed and calculated structure factors for observed reflections* (× 10). *Estimated upper bounds and calculated structure factors for reflections too weak to measure* (× 10)

H	K	FOBS	FCALC
L=0			
2	0	1510	-1911
4	0	1480	-1335
6	0	2779	2665
8	0	1352	-1369
10	0	1072	-1084
12	0	1639	1637
14	0	846	-777
16	0	823	-822
18	0	1110	1146
20	0	458	-485
22	0	408	-423
24	0	652	670
2	1	929	-1027
4	1	1646	1653
8	1	437	-392
10	1	853	868
14	1	725	-771
16	1	516	452
0	2	1911	2033
2	2	1812	-1703
4	2	868	-758
6	2	2500	2463
8	2	1125	-1111
10	2	793	-603
12	2	1178	1142
14	2	531	-400
16	2	702	-593
18	2	868	755
20	2	301	-253
22	2	315	-335
24	2	437	499
2	3	2266	-2727
4	3	2689	2707
6	3	265	159
8	3	2031	-1890
10	3	1812	1742
14	3	1042	-990
16	3	1012	950
20	3	921	-885
22	3	524	622
0	4	583	580
2	4	481	-528
4	4	186	-140
6	4	574	-498
10	4	258	209
2	5	2054	-2239
4	5	2049	2122
6	5	459	-405
8	5	1503	-1492
10	5	1321	1291
14	5	1367	-1265
16	5	929	890
20	5	738	-597
22	5	487	553
0	6	2016	-2109
2	6	815	784
4	6	951	975
6	6	1306	-1337
8	6	695	604
10	6	762	696
12	6	1238	-1169
14	6	537	528
16	6	330	337
18	6	815	-702
24	6	408	-348
2	7	770	-808
4	7	595	618
6	7	265	-173
8	7	559	-572
10	7	401	325
0	8	1404	-1478
2	8	981	1025
4	8	929	967
6	8	1722	-1841
8	8	823	805
10	8	745	681
12	8	1329	-1318
14	8	473	497
16	8	394	459
18	8	929	-800
24	8	416	-475
2	9	694	626
4	9	373	-411
8	9	778	765
10	9	587	-521
14	9	301	286
16	9	315	-375
0	10	1178	-1207
2	10	559	506
4	10	494	486
6	10	793	-780
8	10	279	373
12	10	762	-660
18	10	438	-474
2	11	1057	1020
4	11	1004	-964
8	11	1034	970
10	11	861	-856
14	11	883	792
16	11	724	-655
20	11	409	338
2	13	823	755
4	13	793	-700
8	13	823	750
10	13	778	-677
0	14	416	544
6	14	778	700
12	14	516	547
0	16	531	723
6	16	531	608
L=1			
1	0	1646	1788
2	0	1208	-1117
3	0	3361	-3554
5	0	1004	1000
6	0	585	-473
7	0	1639	1606
8	0	376	-283
9	0	2243	-2345
11	0	997	1009
13	0	936	962
15	0	1442	-1506
17	0	883	794
0	1	299	230
1	1	1344	-1225
2	1	345	349
3	1	220	244
4	1	491	443
5	1	672	689
7	1	997	-987
11	1	731	775
13	1	685	-689
1	2	913	823
3	2	1684	-1815
4	2	722	761
5	2	778	831
7	2	1185	1220
9	2	1843	-1934
11	2	830	859
15	2	891	-1015
0	3	335	-331
1	3	2220	-2333
2	3	655	551
3	3	687	-505
5	3	2122	2406
7	3	1948	-2076
11	3	1291	1490
13	3	1246	-1315
0	5	549	-521
1	5	1986	-1879
5	5	1850	1827
7	5	1608	-1597
11	5	1397	1527
13	5	1216	-1266
1	6	1095	-1009
3	6	1805	1818
5	6	753	-819
7	6	623	-617
9	6	1133	1138
5	7	730	754
1	8	989	-907
3	8	1616	1719
5	8	846	-927
7	8	830	-813
9	8	1442	1530
1	9	808	707
1	10	631	-528
3	10	891	969
1	11	1034	1142
L=2			
0	0	2870	2959
2	0	2039	-2068
3	0	326	-378
4	0	1518	-1404
5	0	981	967
6	0	2417	2592
8	0	906	-910
10	0	1012	-926
11	0	573	607
12	0	1488	1605
13	0	442	-428
14	0	701	-643
16	0	589	-582
18	0	1148	1076
1	1	326	-257
2	1	785	-842
4	1	815	905
6	1	441	-401
8	1	861	-898
10	1	555	633
14	1	457	-502
16	1	478	435
0	2	2001	2168
4	2	966	-895
6	2	1639	1606
8	2	1012	-1013
10	2	688	-596
12	2	1178	1190
1	3	567	-506
2	3	2522	-2401
3	3	451	452
4	3	2039	1969
8	3	1729	-1662
10	3	1480	1387
14	3	1133	-1101
16	3	981	894
2	5	1827	-1680
3	5	543	475
4	5	2016	1863
8	5	1472	-1405
10	5	1216	1319
14	5	846	-981
16	5	743	821
0	6	1503	-1505
1	6	534	398
2	6	861	848
4	6	704	734
6	6	1435	-1421
10	6	598	602
12	6	989	-945
2	7	667	-649
4	7	608	593
0	8	1843	-1745
1	8	506	440
2	8	701	687
4	8	745	797
6	8	1571	-1506
8	8	929	803
12	8	1284	-1165
0	10	747	-898
2	11	944	912
L=3			
1	0	1435	1395
2	0	936	-811
3	0	1956	-2266
4	0	1057	1073
5	0	1269	1194
7	0	1117	1114
8	0	574	-588
9	0	1624	-1740
10	0	558	483
11	0	649	653
13	0	654	579
15	0	1231	-1228
17	0	509	458
1	1	725	-711
5	1	669	735
6	1	436	-450
7	1	707	-665
11	1	637	662
13	1	468	-408
1	2	929	836
2	2	785	-750
3	2	1472	-1502
4	2	614	623
5	2	702	748
7	2	475	572
9	2	1253	-1288
15	2	687	-793
0	3	1208	-1135
1	3	1767	-1820
2	3	653	596
5	3	1812	1821
6	3	616	-605
7	3	1420	-1322
11	3	1216	1169
12	3	546	-477
13	3	1042	-1036
17	3	793	757
0	5	707	-677
1	5	1586	-1523
5	5	1450	1266
6	5	648	-700
7	5	1480	-1451
11	5	1027	1085
13	5	966	-906
1	6	669	-634
3	6	1442	1325
5	6	580	-596
7	6	637	-639
9	6	1027	973
15	6	666	707
0	7	511	-444
1	7	616	-533
1	8	735	-673
3	8	1578	1456
5	8	726	-646
7	8	635	-599
9	8	1420	1214
1	9	566	519
1	10	472	-389
1	11	861	858
L=4			
0	0	1767	1850
1	0	649	-698
2	0	808	-791
4	0	1012	-1095
5	0	906	910
6	0	1563	1618
7	0	808	-870
8	0	720	-715
10	0	702	-717
11	0	588	572
12	0	1193	1286
13	0	544	-634
14	0	559	-554
16	0	413	-409
3	1	287	358
4	1	472	545
8	1	447	-532
9	1	385	429
10	1	637	509
0	2	1034	1062
1	2	577	-571
2	2	575	-614
4	2	478	-549
5	2	429	457
6	2	1231	1189
8	2	484	-477
10	2	504	-568
11	2	506	564
12	2	725	906
1	3	324	-388
2	3	1420	-1420
3	3	883	962
4	3	1359	1297
7	3	399	-420
8	3	1102	-1239
9	3	513	610
10	3	997	996
14	3	700	-790
2	5	1072	-1156
3	5	518	602
4	5	1163	1130
8	5	959	-1057
9	5	651	788
10	5	981	1014
14	5	734	-796
0	6	1140	-1186
1	6	580	493
4	6	580	571
5	6	511	-561
6	6	861	-931
12	6	629	-693
0	8	1170	-1198
1	8	685	636
2	8	620	639
4	8	555	517
5	8	619	-503
6	8	1125	-1150
12	8	913	-861
L=5			
1	0	888	775
2	0	913	-951
3	0	1344	-1507
4	0	815	881
5	0	669	644
7	0	534	529
8	0	643	-670
9	0	1066	-1084
10	0	589	721
11	0	447	514
1	1	550	-438
1	2	536	431
2	2	525	-557
3	2	1027	-1018
4	2	682	667
5	2	778	621
9	2	665	-689
10	2	578	435
0	3	1042	-1025
1	3	1238	-1203
2	3	486	476
5	3	929	937
6	3	762	-820
7	3	1065	-965
11	3	823	769
0	5	750	-755
1	5	1049	-975
5	5	1027	949
6	5	913	-744
7	5	921	-847
1	6	582	-474
3	6	746	793
9	6	726	744
0	7	393	-311
1	7	468	-432
3	8	929	945
9	8	741	821
L=6			
0	0	921	981
1	0	921	-917
2	0	311	-370
4	0	574	-585
5	0	732	813
6	0	1087	1041
7	0	717	-747
8	0	416	-421
11	0	598	636
12	0	959	773
4	1	337	346
0	2	580	690
1	2	580	-575
2	2	339	-321
4	2	344	-356
5	2	543	555
6	2	605	630
7	2	540	-549
12	2	626	613
1	3	543	-481
2	3	876	-820
3	3	868	878
4	3	785	777
5	3	457	-432
8	3	694	-680
9	3	823	735
10	3	660	641
2	5	793	-684
3	5	883	793
4	5	755	636
8	5	778	-755
9	5	676	653
10	5	717	631
0	6	645	-650
1	6	634	549
5	6	509	-499
6	6	651	-634
7	6	554	465
0	8	921	-795
1	8	707	611
5	8	686	-596
6	8	796	-682

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* Since the completion of the manuscript of this paper, an accurate redetermination of the structure of tellurite (Beyer, Sahl & Zemann, 1965) has come to our attention.

Table 2 (*cont.*)

H	K	EUB	FCAL	H	K	EUB	FCAL	H	K	EUB	FCAL	H	K	EUB	FCAL	H	K	EUB	FCAL	H	K	EUB	FCAL	H	K	EUB	FCAL	H	K	EUB	FCAL	H	K	EUB	FCAL	H	K	EUB	FCAL
				6	15	377	-29	10	5	554	-28	13	1	528	17	6	7	604	123	14	3	567	223	2	10	611	240	8	6	461	458	3	4	424	17	10	1	466	344
		L=0		8	15	377	162	12	5	597	-119	15	1	528	174	7	7	604	-146	15	3	590	-11	3	10	616	796	9	6	475	-20	4	4	438	-80	11	1	490	-190
				10	15	377	-169	14	5	643	111	17	1	528	36	8	7	604	-347	16	3	614	254	4	10	621	-293	10	6	490	367	5	4	455	-05	12	1	513	-02
26	0	370	-271	12	15	377	-23	2	6	476	310	1	2	302	-204	9	7	604	167	18	3	660	-319	0	11	650	262	11	6	506	-278	6	4	475	-13	13	1	536	-130
6	1	151	55	2	16	370	-292	4	6	494	31	3	2	275	66	10	7	604	379	1	4	355	-194	2	11	653	-93	13	6	539	293	7	4	494	-80	14	1	558	-203
12	1	219	68	4	16	377	-352	6	6	516	-70	5	2	322	401	11	7	604	-50	2	4	360	21	3	11	655	02	1	7	436	-161	8	4	517	06	3	2	302	94
18	1	287	34	8	16	377	-266	8	6	548	146	7	2	368	-294	12	7	604	-53	3	4	370	-143					2	7	438	-382	9	4	536	43	8	2	426	-266
20	1	309	-250	10	16	377	-333	10	6	586	-243	9	2	417	-173	13	7	604	-114	4	4	383	141			L=4		3	7	443	205	10	4	561	-44	9	2	451	-03
22	1	332	204					11	6	604	-465	11	2	464	431	3	8	515	-78	5	4	399	-80					4	7	450	342	2	5	460	420	10	2	476	-365
24	1	355	-23			L=1		12	6	604	23	13	2	513	-387	5	8	531	-246	6	4	415	-43	3	0	302	-182	5	7	459	-54	3	5	469	52	11	2	498	435
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24	3	355	-11	10	0	473	153	1	7	579	-426	16	2	528	-501	10	8	590	659	9	4	472	155	1	1	302	-78	8	7	490	-388	9	5	604	79	6	3	404	74
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16	4	279	50	6	1	364	-78	6	7	557	-85	7	3	392	-313	2	9	552	581	13	4	558	07	11	1	424	-204	12	7	546	43	5	6	536	-289	1	4	374	-22
18	4	302	66	8	1	421	30	7	7	604	-470	9	3	435	525	3	9	557	-293	14	4	582	112	12	1	453	-49	13	7	561	-85	6	6	550	-47	2	4	379	63
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22	4	475	-13	10	1	476	-201	9	7	604	-56	12	3	503	-138	5	9	604	176	2	5	404	387	14	1	453	-413	7	8	509	462	8	6	581	464	4	4	404	-88
12	5	249	-03	12	1	531	-216	10	7	604	98	13	3	523	-165	6	9	604	-167	3	5	413	03	15	1	453	121	8	8	520	516	10	6	617	-446	5	4	419	-37
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14	7	294	-183	6	2	381	-201	8	8	623	127	3	4	358	-451	2	10	592	509	14	5	601	97	15	2	528	40	2	9	604	459	7	7	603	-257	11	4	531	-33
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22	8	370	300	14	2	592	-119	0	9	606	116	8	4	438	180	6	0	334	-70	8	6	514	506	13	3	486	-324			L=5		2	8	598	589	11	5	550	-349
6	9	219	-102	16	2	646	85	2	9	611	53	9	4	456	-119	12	0	494	-58	10	6	546	-363	15	3	528	536					4	8	609	-612	2	6	466	324
12	9	302	52	4	3	366	85	3	9	614	-04	10	4	477	-01	14	0	543	-302	11	6	564	-429	0	4	317	20	6	0	382	55	5	8	617	-514	3	6	471	66
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14	10	332	274	10	3	505	170	7	9	679	544	14	4	561	-11	3	1	302	170	16	6	663	-228	4	4	345	-92	3	1	302	-22	10	8	679	-474	2	7	506	-253
16	10	347	266	12	3	554	-167	8	9	679	-30	15	4	585	74	4	1	282	127	2	7	488	296	5	4	358	200	4	1	321	180	0	9	679	287	3	7	511	277
6	11	302	-26	14	3	606	-33	9	9	679	-86	16	4	608	-12	8	1	394	300	3	7	494	-72	6	4	374	-66	5	1	358	454	1	9	679	311	4	7	518	176
12	11	332	15	15	3	604	91	10	9	679	-161	1	5	386	-70	9	1	420	92	4	7	501	41	7	4	390	85	6	1	388	-389	2	9	679	-164	5	7	525	-130
18	11	370	28	1	4	378	243	2	10	654	176	5	5	420	-35	10	1	446	157	5	7	509	456	8	4	408	40	7	1	422	-463	3	9	679	31	6	7	536	49
0	12	309	136	2	4	383	-188	4	10	666	-29	6	5	433	-173	12	1	404	-163	6	7	519	-113	9	4	424	-01	8	1	450	222	4	9	679	-150	7	7	546	-105
2	12	309	-59	3	4	395	187	0	11	698	110	7	5	448	-386	14	1	604	51	7	7	533	-404	10	4	443	-11	9	1	480	25	5	9	679	-332	8	7	558	-254
4	12	317	-102	5	4	424	-234	2	11	701	08	9	5	482	508	15	1	604	-18	8	7	546	46	11	4	463	15	10	1	508	122					2	8	543	439
6	12	317	-03	6	4	441	113					11	5	521	-348	16	1	604	55	9	7	561	-57	12	4	481	-12	11	1	536	300			L=6		3	8	548	-49
8	12	324	-01	7	4	462	104			L=2		12	5	541	159	17	1	604	323	10	7	577	-21	13	4	500	-09	12	1	604	-281					4	8	553	359
10	12	332	-46	8	4	481	312					13	5	561	-165	6	2	358	-303	11	7	592	262	14	4	520	-35	6	2	410	-91	3	0	377	-58	7	8	577	590
12	12	347	123	9	4	505	64	1	0	302	-207	15	5	603	258	8	2	407	-175	12	7	611	-85	15	4	538	52	7	2	438	350	9	0	436	45	8	8	587	323
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6	13	339	-109	11	4	551	-128	9	0	402	99	3	6	438	88	11	2	480	563	2	8	530	539	5	5	390	-335	11	2	547	280	13	0	531	-560	2	9	604	326
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14	13	370	460	13	4	604	-31	17	0	601	165	7	6	482	335	13	2	530	527	6	8	558	57	7	5	417	-412	3	3	374	24	1	1	377	-173	4	9	604	-304
16	13	377	-456	14	4	604	57	19	0	650	-238	8	6	495	469	14	2	553	-347	8	8	582	381	11	5	484	-306	4	3	394	382	2	1	377	-293				
2	14	347	-286	2	5	430	61	3	1	302	46	9	6	513	-88	16	2	603	227	10	8	608	-400	12	5	500	-18	8	3	487	361	3	1	377	367				
4	14	347	-352	3	5	438	122	5	1	302	-116	11	6	546	-161	3	3	329	-00	0	9	567	200	13	5	518	-198	9	3	511	-55	5	1	330	-196				
8	14	355	-306	4	5	450	100	7	1	355	-234	13	6	585	140	4	3	345	322	2	9	571	-85	15	5	555	429	10	3	536	376	6	1	359	46				
10	14	362	-301	6	5	479	-292	9	1	407	322	1	7	469	-12	8	3	428	245	3	9	574	61	2	6	401	506	12	3	586	-573	7	1	386	-168				
2	15	377	167	8	5	513	149	11	1	456	-168	3	7	477	140	9	3	449	49	4	9	580	-163	3	6	408	-21	1	4	405	118	8	1	414	-340				
4	15	377	-192	9	5	534	-42	12	1	332	127	5	7	492	52	10	3	472	191	5	9	587	-479	7	6	447	474	2	4	413	-66	9	1	441	316				

Table 3. *Interatomic distances and angles*

Estimated standard deviations are in parentheses

Te–O(2)	1·879 (16) Å	O(2)–O(2′)	2·549 (23) Å
Te–O(2′)	2·018 (16)	O(3)–O(4)	2·456 (33)
Te–O(3)	1·950 (12)	O(2)–O(3)	2·933 (24)
Te–O(4)	2·164 (17)	O(2)–O(4)	2·734 (25)
		O(3)–O(2′)	2·571 (23)
Te–O(2″)	2·800 (16)		
Te–O(6′)	2·828 (7)	N–O(6)	1·194 (34)
Te–O(7″)	2·888 (23)	N–O(7)	1·268 (25)
		O(3)–O(6)	2·754 (31)
Te–Te′	3·270 (2)	O(7)–O(7′)	2·175 (33)
Te–Te″	3·475 (2)	O(6)–O(7)	2·139 (28)
O(2)–Te–O(2′)	81·6 (0·7)°	Te–O(2)–Te″	126·2 (0·8)°
O(2)–Te–O(3)	100·0 (0·8)	Te–O(2′)–Te‴	126·2 (0·8)
O(2)–Te–O(4)	84·8 (0·9)	Te–O(3)–Te′	114·0 (1·0)
O(3)–Te–O(4)	73·1 (1·0)	Te–O(4)–Te′	98·2 (1·1)
O(3)–Te–O(2′)	80·7 (0·8)		
O(4)–Te–O(2′)	147·8 (0·8)	O(6)–N–O(7)	120·6 (1·1)
		O(7)–N–O(7′)	118·1 (1·6)
		N–O(6)···O(3)	97·0 (2·1)

atom is found in all three compounds. In each compound there are also several tellurium–oxygen distances of intermediate length (two at 2·89 Å in α-TeO_2, three in $Te_2O_4.HNO_3$ at 2·80, 2·83 and 2·89 Å, in tellurite two at 2·7 and 2·8 Å), which do not seem to form a meaningful pattern.

The salient features of each structure suggest a distorted trigonal bipyramid of oxygen atoms around each tellurium, with a lone pair of electrons occupying one of the equatorial positions. In the case of $Te_2O_4.HNO_3$, O(4) and O(2′) occupy axial positions, O(2) and O(3) occupy two of the equatorial positions, and the lone pair of electrons occupies the third equatorial position. The average of all four shortest tellurium–oxygen distances is 2·003 Å in both $Te_2O_4.HNO_3$ and α-TeO_2. The differences among the four shortest tellurium–oxygen bonds may be rationalized in the following way. In the first place, the fact that the axial bonds are longer than the equatorial bonds in both $Te_2O_4.HNO_3$ and α-TeO_2 can be interpreted in terms of different hybrids used by tellurium for the two kinds of bond; *e.g.* $5s\ 5p_x\ 5p_y$ for equatorial bonds, $6s\ 5p_z$ for axial bonds, would lead to the observed difference. In the second place, tellurium–oxygen bonds within the four-membered Te_2O_2 rings in $Te_2O_4.HNO_3$ are longer than those outside, consistent with a postulated strain in the rings. Further, the strain in a particular part of either structure seems to be measured by the deviation of the tellurium–oxygen–tellurium angle from an ideal value, apparently near 126°. The effect of the strain on the bond lengths is slightly less than the effect of hybridization.

The intermediate-length tellurium–oxygen distances could suggest weak bonding, but the lack of some coherent pattern in the different compounds makes this approach uncertain. Alternatively, the van der Waals radius of a tellurium atom bonded to four more electronegative atoms should be considerably less than the usual 2·2 Å value based on the ionic radius of Te^{2-} (Pauling, 1960). A value of about 1·74 Å is consistent with the experimental distances, and then no tellurium–tellurium bonding need be postulated.

The distance between O(6) and O(3) is 2·75 Å and the angle N–O(6)···O(3) is 97°, indicating a fairly strong hydrogen bond, O(6)–H···O(3). The infrared spectrum confirms the presence of hydrogen bonding. In each spectrum a rather broad (half width $\simeq 300\,cm^{-1}$) and intense ($\simeq 40\%$ absorption) peak centered near 250 cm3^{-1} was observed. For an interaction of the type O–H···O, this would imply an O–H···O distance of approximately 2·74–2·76 Å (Nakamoto, Margoshes & Rundle, 1955).

The authors wish to express their thanks to Mr B. Annis, Mr L.A.Chasin, and Mr W.S.Magee (former students at Brown) for collecting the data and for preliminary calculations, to Dr C.K.Johnson (Oak

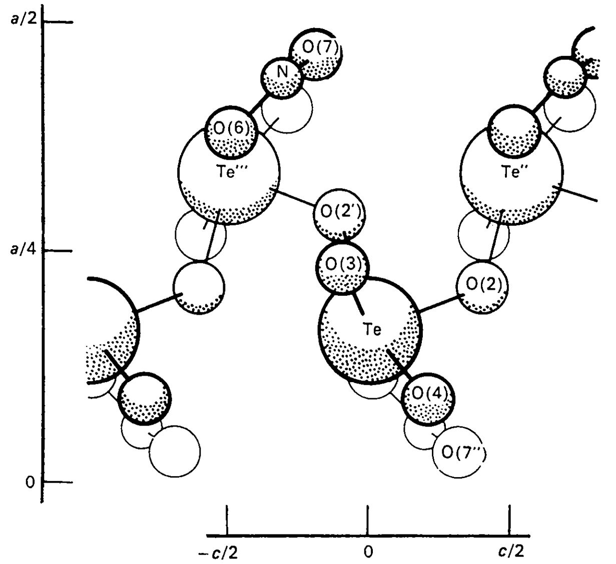

Fig. 2. The section of one layer between mirror planes projected along the *b* axis.

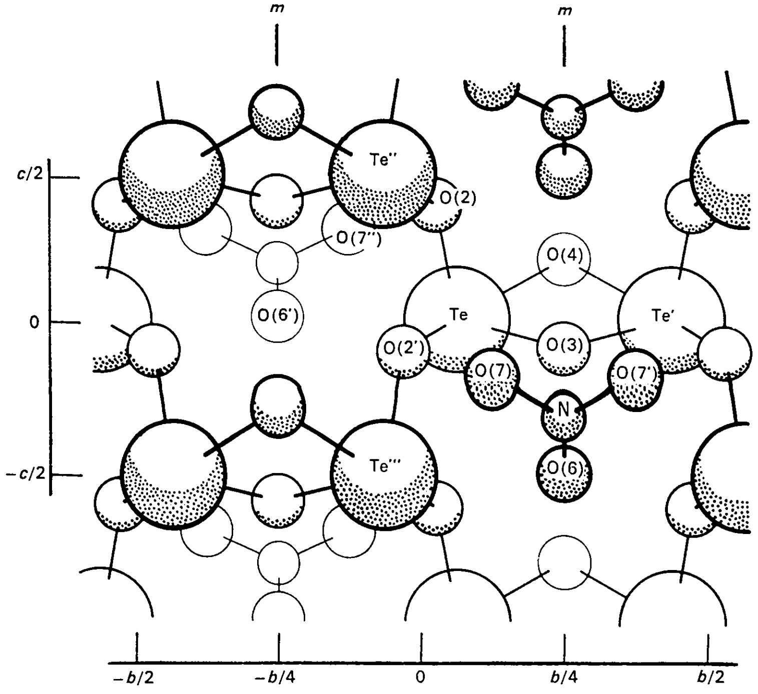

Fig. 1. A section of one layer projected along the *a* axis.

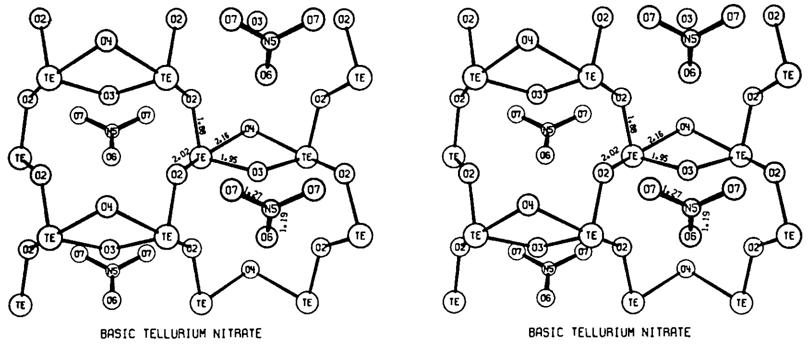

Fig. 3. Stereoscopic drawing of a section of one layer as viewed from the *a* axis.

Ridge) for the stereoscopic drawing (Fig. 3) and slide used at the Gatlinburg ACA meeting, and to Professor J. O. Edwards (Brown) who suggested this problem.

This work was supported in part by the Office of Naval Research and in part by the Advanced Research Projects Agency.

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Die Struktur von $Na_2H_2SiO_4.4H_2O$

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(*Eingegangen am* 14. *Januar* 1966)

$Na_2H_2SiO_4.4H_2O$ crystallizes in space group $P\bar{1}$, with the cell dimensions

$$a=7{\cdot}96,\quad b=9{\cdot}61,\quad c=6{\cdot}67\text{ Å};$$
$$\alpha=70{\cdot}1,\quad \beta=104{\cdot}3,\quad \gamma=122{\cdot}5°.$$

The structure was determined by direct methods. Isolated SiO_4 tetrahedra are linked by hydrogen bonds to form layers which are separated by layers of Na and H_2O. The problem of the condensation of single SiO_4 tetrahedra to pairs, Si_2O_7, during solution is discussed.

Einleitung

Thilo, Wieker & Stade (1965) entwickelten eine Methode zur Bestimmung des Kondensationsgrades löslicher Silicate. Als Mass für den Kondensationsgrad nehmen sie die Geschwindigkeit, mit der sich Silicomolybdat bildet, wenn ein in Säuren leicht lösliches Silicat oder eine frisch hergestellte Silicat-Lösung in eine saure Lösung von Ammoniummolybdat gebracht werden. Die Temperatur, bei der üblicherweise gearbeitet wird, ist +25°C. Einige Silicate, vor allem das $Na_2O.SiO_2.5H_2O$ zeigen jedoch bei dieser Reaktion ein bemerkenswertes Verhalten: Löst man das $Na_2O.SiO_2.5H_2O$ bei +2°C, so verhält es sich bei der Molybdat-Reaktion wie ein Monosilicat, löst man es bei +25°C, so verhält es sich wie eine Mischung aus Mono- und