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ON THE POLYMORPHISM OF ORTHOTELLURIC ACID, H_6TeO_6

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SUMMARY

The preparation of the various modifications of orthotelluric acid is described. In addition to the previously known monoclinic and cubic modifications, a third form—tetragonal H_6TeO_6—could be prepared. Unit cell data have been derived from X-ray single crystal study:

H_6TeO_6 (monoclinic): $a = 6.49_4$ Å, $b = 9.32_2$ Å, $c = 8.33_3$ Å, $\beta = 99°43'$.
H_6TeO_6 (cubic) : $a = 15.69_5$ Å.
H_6TeO_6 (tetragonal) : $a = 15.65_2$ Å, $c = 15.76_2$ Å.

Indexed powder patterns are listed for all three polymorphic forms. The discrepancies found in the literature dealing with orthotelluric acid are pointed out. Monoclinic H_6TeO_6 is the most stable form. Cubic H_6TeO_6 transforms at elevated temperatures (*e.g.*, 90°–110°C) to tetragonal H_6TeO_6 in dry atmosphere and to monoclinic H_6TeO_6 in water vapor-containing atmosphere. I.R. spectra and DTA/TGA investigations are discussed briefly.

INTRODUCTION

It is generally accepted that orthotelluric acid crystallizes in two forms, monoclinic and cubic H_6TeO_6. In many papers which describe I.R. spectra, thermal decomposition, or reactions of H_6TeO_6, it is not stated which form of orthotelluric acid was actually prepared and used for the study. This may be due partly to the fact that reliable X-ray powder patterns for identification of the H_6TeO_6-modifications are not available so far. All the powder patterns listed in the literature[5,7-10] are either very inaccurate with regard to the *d*-spacings and to splitting of reflections, or they refer to a mixture of both modifications. Weaker reflections are not listed at all. So far no structure determination has been carried out on any of the modifications.

During investigations into the crystal chemistry of Te-containing oxide compounds[12], the preparation and dehydration of H_6TeO_6 was studied. It was found possible to prepare and to characterize three modifications of orthotelluric acid, *viz.*, cubic, tetragonal and monoclinic. X-ray powder patterns of all three forms are given in this paper. Before presenting these results it is necessary to discuss briefly previous work dealing with the modifications of H_6TeO_6 and to point out the many discrepancies. This should not be regarded as criticism since the scope of some of these investigations was somewhat different to the one here reported and adequate X-ray equipment was probably not available.

LITERATURE REVIEW

KIRKPATRICK AND PAULING[1] were the first to study cubic H_6TeO_6 by single crystal X-ray techniques. Their data concerning the size of the unit cell and the space group are essentially still valid and agree with those of the author. There is some deviation in the magnitude of the lattice constant (PAULING: $a = 15.48$ Å, present study: $a = 15.69_5$ Å) which may be explained by the higher precision of the author's powder data. KIRKPATRICK AND PAULING also only observed reflections with $h = 2n$, $k = 2n$ (for hko), with $h = 2n$ (for $h$oo) and with $h+k$, $k+l = 2n$ (for hkl). There are 32 formula units in the cell, $D_{\text{exp}} = 3.12$ g/cm^3, $D_x = 3.26$ g/cm^3, space group probably $O^8{}_h$-$Fd3c$.

Several years later GOSSNER AND KRAUS[2] studied single crystals of both cubic and monoclinic H_6TeO_6. They rejected PAULING's results for cubic H_6TeO_6 and instead gave a lattice constant, $a = 7.83$ Å. The reason for the discrepancy was that these authors did not observe the relatively weak odd layer reflections which require doubling of their lattice constant. This was stated in PAULING's reply[3] in which he clearly demonstrated that reflections 531, 971, 11.5.1, 11.5.3 exist. The author's single crystal study confirmed the correctness of PAULING's results.

GOSSNER AND KRAUS[2] concentrated their study mainly on monoclinic H_6TeO_6. They determined the following lattice constants: $a = 5.70$ Å, $b = 9.30$ Å, $c = 9.74$ Å, $\beta = 104°30'$, $Z = 4$, $D_x = 3.07$ g/cm^3, space group $C^5{}_{2h}$-$P2_1/c$.

The author's single crystal X-ray study showed that when choosing this setting, the lattice constant a needed to be doubled. This leads to extinctions which are not compatible with the above space group. Therefore a new, smaller unit cell was chosen. These results will be discussed later.

PASSERINI AND ROLLIER[4] reported X-ray studies on cubic H_6TeO_6. Their value for the lattice constant $a = 15.68$ Å (space group $O^8{}_h$-$Fd3c$) comes closest to the value determined from the present studies. The results are in agreement with those reported by PAULING.

The X-ray pattern listed for H_6TeO_6, cubic phase, in the ASTM-card index[5a] corresponds to a mixture of monoclinic and cubic H_6TeO_6. The pattern listed for H_2TeO_4[5b] is very similar to that of monoclinic H_6TeO_6, except for the two first reflections.

SIEBERT[6] reported i.r. data on orthotelluric acid, but did not determine by X-ray, or by microscopy, which modification of H_6TeO_6 he actually studied. The author's i.r. study showed that there are certain characteristic shifts of absorption bands. One important finding of SIEBERT was that orthotelluric acid indeed has the formula $Te(OH)_6$ since no H_2O-deformation frequency (at 1600 cm^{-1}) was found in the i.r. absorption spectrum.

JANDER AND KIENBAUM[7] described the preparation, analysis and reactions of H_6TeO_6 but they also were not concerned about which modification they had prepared. A schematic X-ray pattern given in that paper contains only 10 reflections which correspond roughly to some of the strong reflections of monoclinic H_6TeO_6.

ROSICKY, LOUB AND PAVEL[8] recently investigated the dehydration of orthotelluric acid. The preparation of monoclinic H_6TeO_6 is described, but again only a schematic "line-pattern" is given which obviously corresponds to a mixture of monoclinic and cubic H_6TeO_6.

In a recent thesis on the system TeO_3–H_2O by THA[9] powder patterns of both cubic and monoclinic H_6TeO_6 were listed but were not indexed. Whereas the pattern of cubic H_6TeO_6 is roughly in agreement with the data reported here, the pattern given for the monoclinic form has no similarity to that determined in these investigations. The main part of this thesis is concerned with i.r. studies, dehydration of H_6TeO_6, and with the preparation of H_2TeO_4.

A paper by BREUSOV *et al.*[10] lists *d*-spacings for cubic and for monoclinic orthotelluric acid. The data for cubic H_6TeO_6 agree fairly well with our own results; however, many reflections are missing and the *d*-spacing for the reflection (400) certainly is incorrect. These authors determined the lattice constant to be $a = 15.63$ Å. The *d*-spacings for monoclinic H_6TeO_6 were not indexed and are not very accurate. It is surprising that none of the authors who reported powder data on monoclinic H_6TeO_6 ever observed the very obvious splitting of the first reflections. Powder photographs of the various forms of H_6TeO_6 are shown in a recent paper by the present author[12].

Finally, DUTTON AND COOPER[11] gave a good, but non-critical, review on the oxides and oxyacids of tellurium. They also mentioned the preparation of a sample of H_6TeO_6 which they assumed to be the cubic modification. From this assumption they conclude that the monoclinic form may exist but that the cubic form of orthotelluric acid is more easily obtained. This is in contradiction to this author's results and to those of other authors[3,9,10,12] which showed that monoclinic H_6TeO_6 is the stable form and is easily obtained by crystallization from the aqueous solution.

EXPERIMENTAL RESULTS AND DISCUSSION

Preparation of orthotelluric acid

The various methods for preparation of H_6TeO_6 are summarized by DUTTON AND COOPER[11]. In the present investigation orthotelluric acid was prepared by reacting very pure tellurium (99.999%) with analytical grade, 30% H_2O_2 (Perhydrol, Merck) for several days in the dark. After filtration from unreacted tellurium the H_6TeO_6 solution was diluted with distilled water and boiled in order to destroy excess H_2O_2. The solution was then used for the crystallization experiments. This method of preparation was preferred to other methods described in the literature in order to avoid impurities which might have a stabilizing effect on one of the H_6TeO_6 modifications, three of which could be prepared.

Monoclinic H_6TeO_6 crystallizes readily from the aqueous solution at room temperature. The crystals are usually elongated prisms and show the formation of columnar and sheaf-like aggregates. It is somewhat difficult to find good, small, single crystals for X-ray study. Increasing the crystallization temperature or decreasing the solution depth favors the crystallization of cubic H_6TeO_6 in addition to the monoclinic form.

Cubic H_6TeO_6 could be prepared by one of the following methods:

(1) Rapid evaporation of thin layers of aqueous H_6TeO_6 solution, *e.g.*, on microscopic slides at elevated temperatures (60°–90°C). By this method good single crystals were obtained, mostly in the form of octahedra. Frequently dendritic growth was observed[12].

(2) Rapid precipitation by pouring a diluted H_6TeO_6 solution into acetone or alcohol, preferably at elevated temperatures, *e.g.*, 50°–55°C. After decantation and washing with alcohol the fine crystalline precipitate consists mainly of cubic H_6TeO_6.

(3) Rehydration of amorphous, yellow "α-TeO_3" which was prepared by heating monoclinic H_6TeO_6 for 20 h at 250°C. This "α-TeO_3" rehydrates predominantly to cubic H_6TeO_6 either very slowly at room temperature (*e.g.*, after two months) or after several hours at elevated temperatures and in water vapor (*e.g.*, 70°C, 20 h).

It was not possible to transform monoclinic H_6TeO_6 into cubic H_6TeO_6, *e.g.*, by heating in dry or in moist air in the temperature region 20°–120°C. On the other hand, cubic H_6TeO_6 transforms readily to monoclinic H_6TeO_6 when heated in water vapor, *e.g.*, 20 h at 90°C. The originally octahedral crystals decompose to an aggregate of fine needles of monoclinic H_6TeO_6.

Tetragonal H_6TeO_6 was formed by heating cubic H_6TeO_6 in dry air in the temperature range 90°–110°C (50 h). This modification has not been found previously.

All these results suggest that monoclinic H_6TeO_6 is the stable modification and not cubic H_6TeO_6.

Deuterated orthotelluric acid, D_6TeO_6, was prepared for i.r. study by dissolving tellurium (99.999%) in D_2O_2 (30%)–D_2O, filtration from unreacted Te, and evaporation to dryness. The X-ray pattern of this product was identical to that of monoclinic H_6TeO_6.

A DTA/TGA study showed that the dehydration of the various H_6TeO_6 modifications and of D_6TeO_6 starts at about 130°C and proceeds practically identically[12] in each case. Chemical analysis was not carried out since all DTA/TGA runs up to 600°C gave exactly the weight loss calculated from the reaction $H_6TeO_6 \rightarrow TeO_2$ (tetragonal) $+ 3\ H_2O + \frac{1}{2}\ O_2$.

X-Ray study

X-ray powder diffraction data (Cu *K*-radiation, Guinier Jagodzinski camera, Si as internal standard) for the three modifications of orthotelluric acid are listed in Tables I and II. For determination of the unit cells, single-crystal X-ray study (Mo-radiation, precession camera) was carried out on both cubic and monoclinic H_6TeO_6.

Monoclinic H_6TeO_6. Preliminary single-crystal study was based on the results reported by GOSSNER AND KRAUS[2]. More careful precession study on good single crystals however proved the existence of weak reflections which require doubling of the lattice constant *a* given by those authors, *e.g.*, reflections 501, 303, 307. With this doubled unit cell, extinctions were observed which are not compatible with the monoclinic space group $P\ 2_1/c$. A different setting of the crystal was therefore chosen, leaving the *b* axis unchanged. This leads to a smaller unit cell with *a*, *c* and β different from that given by GOSSNER AND KRAUS[2]. The simple relationship between the new orientation and the previous one by GOSSNER AND KRAUS can be seen from Fig. 1.

The matrix for transformation of the *hkl* given by GOSSNER AND KRAUS (hkl_{GK}) to the *hkl* for the new cell is as follows:

$$\begin{pmatrix} 1 & 0 & \frac{1}{2} \\ 0 & 1 & 0 \\ \bar{1} & 0 & \frac{1}{2} \end{pmatrix} \begin{pmatrix} h_{GK} \\ k_{GK} \\ l_{GK} \end{pmatrix} = \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

TABLE I

X-RAY DATA FOR H_6TeO_6 (MONOCLINIC)

hkl	*d (exp.)*	*d (calc.)*	*Int.*	*hkl*	*d (exp.)*	*d (calc.)*	*Int.*
$11\bar{1}$	4.76	4.750	vs	$11\bar{5}$	1.6355	1.6342	w
020	4.66	4.661	vs	204	1.6088	1.6091	w
111	4.18	4.182	vs	400	1.5998	1.6002	vw
002	4.11	4.106	s	$33\bar{3}$	1.5830	1.5833	w
$11\bar{2}$	3.484	3.484	w	060	1.5535	1.5537	w
200	3.201	3.200	m	313	1.5393	1.5386	m
$022,02\bar{2}$	3.081	3.081	ms	$15\bar{3}$	1.5315	1.5317	w
130	2.795	2.7954	vw	224	1.5209	1.5210	w
$20\bar{2}$	2.760	2.7602	w	420	1.5143	1.5135	vw
$13\bar{1}$	2.7078	2.7079	m	115	1.5097	1.5098	w
220	2.6393	2.6383	s	$42\bar{2}$	1.4997	1.4999	vw
$013,01\bar{3}$	2.6270	2.6267	vw	153	1.4673	1.4668	w
$22\bar{1}$	2.6194	2.6203	vw	$13\bar{5}$	1.4632	1.4641	w
131	2.5895	2.5887	s	$062,06\bar{2}$	1.4530	1.4532	w
$11\bar{3}$	2.5795	2.5813	s	402	1.4125	1.4125	w
221	2.4160	2.4159	vw	$31\bar{5}$	1.4070	1.4065	w
$22\bar{2}$	2.3749	2.3750	wm	260	1.3978	1.3977	w
202	2.3400	2.3400	vw	333	1.3944	1.3942	w
040	2.3305	2.3306	wm	$40\bar{4}$	1.3799	1.3801	vw
113	2.3032	2.3026	wm	135	1.3727	1.3727	w
$041,04\bar{1}$	2.2424	2.2420	vw	314	1.3535	1.3540	w
132	2.2355	2.2354	vw	424	1.3237	1.3233	w
$31\bar{1}$	2.1005	2.1001	w	440	1.3191	1.3192	vw
222	2.0917	2.0913	ms	026	1.3128	1.3133	vw
310	2.0796	2.0798	vw	$35\bar{3}$	1.3096	1.3097	w
004	2.0536	2.0532	m	262	1.2941	1.2944	w
$13\bar{3}$	2.0330	2.0322	w	$51\bar{1}$	1.2865	1.2862	vw
$042,04\bar{2}$	2.0262	2.0268	w	171	1.2810	1.2809	vw
$31\bar{2}$	1.9920	1.9922	vw	$064,06\bar{4}$	1.2392	1.2390	vw
311	1.9422	1.9416	m	$51\bar{3}$	1.2318	1.2320	vw
133	1.8880	1.8876	ms	511	1.2226	1.2229	vw
240	1.8837	1.8840	ms	422	1.2076	1.2079	vw
$024,02\bar{4}$	1.8780	1.8789	ms	315	1.1971	1.1968	m
$31\bar{3}$	1.8047	1.8053	m	206	1.1878	1.1881	vw
$24\bar{2},223$	1.7802	1.7800	m	155	1.1827	1.1828	vw
$33\bar{1}$	1.7713	1.7711	m	$11\bar{7}$	1.1807	1.1806	vw
$15\bar{1}$	1.7666	1.7664	m	404	1.1700	1.1700	vw
$22\bar{4}$	1.7417	1.7421	wm	$24\bar{6}$	1.1638	1.1637	vw
151	1.7316	1.7320	m	226	1.1512	1.1513	vw
331	1.6728	1.6729	m	335	1.1250	1.1249	vw
242	1.6510	1.6513	m	$082,08\bar{2}$	1.1208	1.1210	vw

$a = 6.494 \pm 0.003$ Å.
$b = 9.322 \pm 0.002$ Å.
$c = 8.333 \pm 0.003$ Å.
$\beta = 99°43' \pm 3'$.
$Z = 4$, space group $P2_1$ or $P2_1/m$.
$D_x = 3.067$ g/cm^3.
$D_{exp} = 3.02$ g/cm^3.

TABLE II

X-RAY DATA FOR H_6TeO_6 (TETRAGONAL) AND H_6TeO_6 (CUBIC)

H_6TeO_6 (tetragonal)			*H_6TeO_6 (cubic)*		*H_6TeO_6 (tetragonal)*			*H_6TeO_6 (cubic)*	
hkl	*d (exp.)*	*Int.*	*d (exp.)*	*Int.*	*hkl*	*d (exp.)*	*Int.*	*d (exp.)*	*Int.*
222	4.54	vs	4.54	vs	408	1.7606	m		
004	3.941	s			804	1.7532	m		
400	3.914	vs	3.925	vs	840	1.7495	m	1.7543	vs
224	3.213	vw			448	1.6054	m		
422	3.201	vw	3.199	w	844	1.5996	m	1.6007	vs
404	2.777	s			2.2.10	1.5166	wm		
440	2.767	m	2.774	vs	666	1.5100	wm		
315	2.660	w			10.2.2	1.5068	m	1.5095	vs
513	2.650	w	2.653	ms	808	1.3885	w		
531	2.649	w			880	1.3831	vw	1.3868	wm
620,602	2.477	vw	2.4813	w	6.2.10	1.3300	wm		
206	2.485				10.2.6	1.3255	m	1.3261	vs
226	2.3747	s			10.6.2	1.3230	m		
622	2.3605	vs	2.3660	vs	848	1.3089	m		
444	2.2648	ms	2.2643	ms	884	1.3056	wm	1.3070	s
642			2.0966	vw	12.0.4	1.2400	vw		
317	2.0502	w			12.4.0	1.2376	w	1.2403	m
731,713	2.0388	w	2.0429	ms	6.6.10	1.1989	w		
008	1.9702	w			10.6.6	1.1958	wm	1.1957	ms
800	1.9564	m	1.9618	s	4.4.12	1.1875	w		
626	1.8018	s			12.4.4	1.1812	m	1.1824	ms
662	1.7960	m	1.8001	vs	888	1.1329	vw	1.1321	vw

$a = 15.652 \pm 0.005$ Å.	$a = 15.695 \pm 0.005$ Å.
$c = 15.762 \pm 0.005$ Å.	
$Z = 32$.	$Z = 32$.
$D_x = 3.16$ g/cm^3.	$D_x = 3.15_5$ g/cm^3.

Complete indexing of the powder pattern was possible with this new unit cell data. *d*-spacings were calculated by means of a computer program. Table I shows the good agreement between measured and calculated data.

Cubic H_6TeO_6. Precession photographs confirmed PAULING's earlier results[1,3]. Thus the unit cell of cubic H_6TeO_6 contains 32 formula units and corresponds to a variation of the perovskite structure. This means a 4-fold lattice constant in all three directions of space. Only every second octahedral site is occupied by tellurium, which is surrounded octahedrally by 6 OH. These groups are held together by hydrogen bridges. Since the density of cubic H_6TeO_6 is higher than that of monoclinic H_6TeO_6 it is reasonable to assume that high pressure would favor the transformation of monoclinic to cubic. Table II lists *d*-spacings for both cubic and tetragonal H_6TeO_6. No single-crystal study has been carried out on tetragonal H_6TeO_6 since good crystals have not been obtained so far.

I.r. study

I.R. absorption spectra in the CaF_2-, NaCl- and KBr-region were recorded with a Perkin-Elmer spectrometer, Model 13. Preliminary runs showed that the spectra had better resolution when using the KBr-disc method instead of dispersing the samples in paraffin oil. The ratio was 1 mg sample to 300 mg KBr. After thorough mixing and pressing, the discs were used immediately for observation of the spectra.

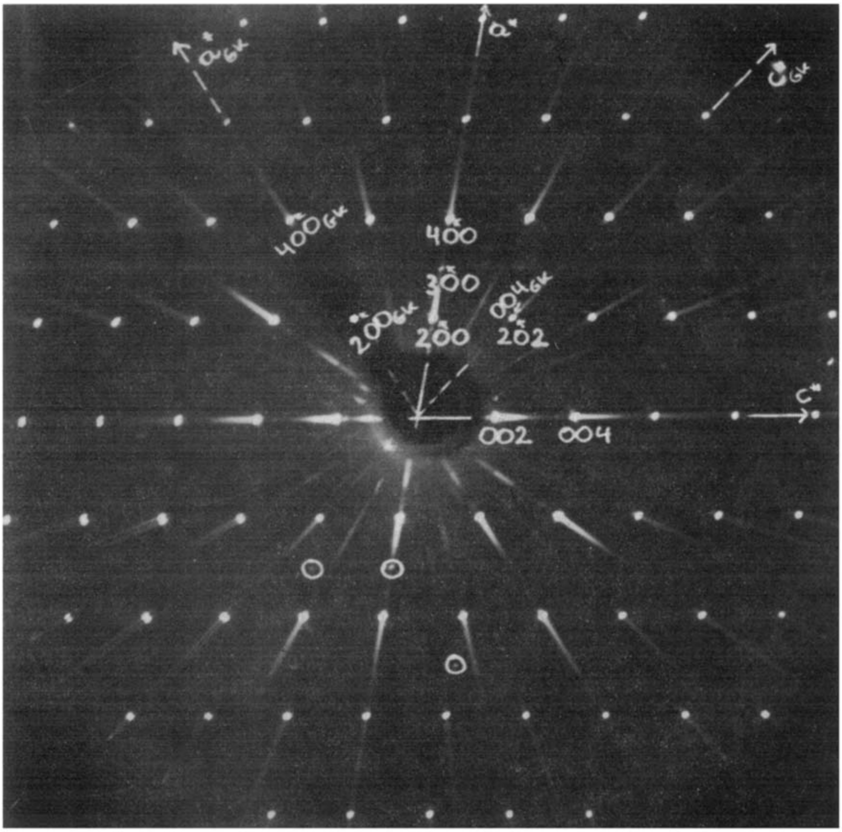

Fig. 1. H_6TeO_6 monoclinic. Zero-level precession photograph, *b*-direction (Mo*K*α-radiation). a_{GK}^*, c_{GK}^* = orientation used by GOSSNER AND KRAUS, a^*, c^* = orientation according to own results. The reflections in circles were omitted by GOSSNER AND KRAUS[3].

A survey of infrared and Raman data on telluric acids is given by DUTTON AND COOPER[11]. I.r. absorption spectra of H_6TeO_6 were reported by SIEBERT[6] and by THA[9]. They agree fairly well with our own data except that these authors did not point out the difference between the spectra of monoclinic and cubic H_6TeO_6. It can

TABLE III

I.R. DATA ON ORTHOTELLURIC ACID

H_6TeO_6 (cubic)	*H_6TeO_6 (monoclinic)*	*D_6TeO_6 (monoclinic)*
3.15 μ, vs(ν-TeOH)	2.95 μ, s(ν-TeOH)	4.30 μ, s(ν-TeOD)
	3.20 μ, vs	
4.4 μ, w(2δ-TeOH)	4.2 μ, w(2δ-TeOH)	
	4.4 μ, w	
8.55 μ, vs(δ-TeOH)	8.20 μ, s(δ-TeOH)	11.15 μ, w(δ-TeOD)
9.35 μ, s	8.45 μ, m	11.60 μ, m
	8.95 μ, s	
14.85 μ, vs(ν-TeO)	14.00 μ, m(ν-TeO)	14.00 μ, m(ν-TeO)
15.05 μ, vs	14.80 μ, vs	14.80 μ, vs
	15.00 μ, vs	15.00 μ, vs

be seen from Table III that there are characteristic shifts and splitting of the ν-TeOH and of the δ-TeOH vibrations. The latter is shifted to longer wavelengths in cubic H_6TeO_6. The i.r. absorption spectrum of cubic H_6TeO_6 shows less splitting and the bands are narrower than in monoclinic H_6TeO_6. This indicates a more symmetrical arrangement in the $Te(OH)_6$-octahedra of cubic H_6TeO_6. The i.r. absorption spectrum of D_6TeO_6 (monoclinic) shows that the TeOD vibrations are shifted by a factor of about 1.36 to longer wavelengths as compared to TeOH. This is in agreement with the results found by THA[9]. The D_6TeO_6 spectrum also contained the ν-TeOH and δ-TeOH vibrations due to the exchange OD → OH in the KBr disc.

DTA/TGA study

A Mettler thermoanalyzer was used for these experiments. All runs were carried out in dry air (flow rate 6 l/h, heating rate 2°C/min, sample weight 30–40 mg). DTA/TGA curves for cubic and monoclinic H_6TeO_6 and also for D_6TeO_6 are almost identical. Loss of H_2O (D_2O) and of O_2, and crystallization of tetragonal TeO_2 occur at about the same temperatures[12]. No transformation of cubic to monoclinic H_6TeO_6 or *vice versa* could be found under these conditions in the temperature range 20°–120°C. One interesting result was that two intermediate, crystalline oxides—TeO_3 and Te_2O_5—could be prepared in the course of these dehydration studies. X-ray patterns of these tellurium oxides are being evaluated at present and will be reported in a separate paper.

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