Preparation, Thermal Behaviour and Crystal Structure of the Basic Mercury(II) Tetraoxotellurate(VI), Hg_2TeO_5, and Redetermination of the Crystal Structure of Mercury(II) Orthotellurate(VI), Hg_3TeO_6

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Abstract. Single crystals of Hg_2TeO_5 were obtained as dark-red parallelepipeds by reacting stoichiometric amounts of $Hg(NO_3)_2 \cdot H_2O$ and H_6TeO_6 under hydrothermal conditions (250 °C, 10d). The crystal structure (space group $Pna2_1$, $Z = 4$, $a = 7.3462(16)$, $b = 5.8635(12)$, $c = 9.969(2)$ Å, 1261 structure factors, 50 parameters, $R[F^2 > 2\sigma(F^2)] = 0.0295$) is characterized by corner-sharing $[TeO_6]$ octahedra forming isolated chains $^1_\infty[TeO_{4/1}O_{2/2}]$ which extend parallel to [100]. The two crystallographically independent Hg atoms are located in-between the chains and interconnect the chains *via* common oxygen atoms. Amber coloured single crystals of Hg_3TeO_6 were prepared by heating a mixture of Hg, HgO and TeO_3 together with small amounts of $HgCl_2$ as mineralizer in an evacuated and sealed silica glass tube (520 °C). The previously reported crystal structure has been re-investigated by means of single crystal *X*-ray data which reveal a symmetry reduction from $Ia\bar{3}d$ to $Ia\bar{3}$ ($Z = 16$, $a = 13.3808(6)$ Å, 609 structure factors, 33 parameters, $R[F^2 > 2\sigma(F^2)] = 0.0221$). The crystal structure is made up of a body-centred packing of $[TeO_6]$ octahedra with the Hg atoms situated in the interstices of this arrangement. Upon heating, both title compounds decompose in a one-step mechanism under formation of TeO_2 and loss of the appropriate amounts of elementary mercury and oxygen.

Keywords: Mercury; Tellurium; Crystal structure

Präparation, thermisches Verhalten und Kristallstruktur des basischen Quecksilber(II)-tetraoxotellurates(VI), Hg_2TeO_5, und Neubestimmung der Kristallstruktur des Quecksilber(II)-orthotellurates(VI), Hg_3TeO_6

Inhaltsübersicht. Einkristalle von Hg_2TeO_5 wurden als dunkelrote Quader durch Umsetzung von stöchiometrischen Mengen an $Hg(NO_3)_2 \cdot H_2O$ und H_6TeO_6 unter hydrothermalen Bedingungen erhalten (250 °C, 10d). Die Kristallstruktur (Raumgruppe $Pna2_1$, $Z = 4$, $a = 7.3462(16)$, $b = 5.8635(12)$, $c = 9.969(2)$ Å, 1261 Strukturfaktoren, 50 Parameter, $R[F^2 > 2\sigma(F^2)] = 0.0295$) besteht aus eckenverknüpften $[TeO_6]$-Oktaedern, die sich in Form isolierter $^1_\infty[TeO_{4/1}O_{2/2}]$-Ketten parallel zu [100] ausbreiten. Die zwei kristallographisch unabhängigen Hg-Atome liegen zwischen den Ketten und verknüpfen diese über gemeinsame Sauerstoffatome. Bernsteinfarbene Einkristalle von Hg_3TeO_6 wurden durch Tempern eines Gemenges an Hg, HgO und TeO_3 zusammen mit Spuren von $HgCl_2$ als Mineralisator in geschlossenen Kieselglasampullen erhalten (520 °C). Die früher beschriebene Kristallstruktur wurde aufgrund einer Symmetrieerniedrigung von $Ia\bar{3}d$ nach $Ia\bar{3}$ ($Z = 16$, $a = 13.3808(6)$ Å, 609 Strukturfaktoren, 33 Parameter, $R[F^2 > 2\sigma(F^2)] = 0.0221$) neu bestimmt und besteht aus einer raumzentrierten Packung von $[TeO_6]$-Oktaedern und in den Zwischenräumen dieser Anordnung sitzenden Quecksilberatomen. Beim Erhitzen der beiden Titelverbindungen entsteht unter Abgabe entsprechender Mengen an elementarem Quecksilber und Sauerstoff TeO_2 ohne intermediäre Bildung anderer Phasen im System Hg/Te/O.

Introduction

During a previous investigation of the ternary system Hg/Te/O many phases with both mercury and tellurium in different oxidation states have been prepared by conventional solid state techniques and characterized by *X*-ray powder diffraction (XRPD) and microprobe analyses [1]. The following phases were postulated by the authors: The mercuric tellurites(IV), $HgTeO_3$ and $HgTe_2O_5$, the mercuric tellurates(VI), $HgTeO_4$, $Hg_3Te_2O_9$ and Hg_3TeO_6, the mercurous tellurate(VI), Hg_2TeO_4, which was also described as the synthetic mineral *magnolite*, as well as the mixed-valent mercuric tellurite(IV) tellurates(VI), $Hg_2Te_2O_7$ and $HgTe_2O_6$. During a later performed single crystal structure analysis of *magnolite* [2] it was evidenced that the primarily assumed formula had to be revised from Hg_2TeO_4 to Hg_2TeO_3, and therefore the very rare mineral has to be classified as a mercury(I) tellurite(VI) and not as a tellurate(VI). Except for $HgTeO_3$ (four-circle diffractometer data) [3] and Hg_3TeO_6, whose structure has been solved from single crystal Weissenberg data [4], no structure or crystallographic data for the other Hg-Te-O phases described in [1] or in the Gmelin handbook on mercury [5] are published so far. For a more detailed understanding of the crystal chemistry of mercury oxotellurium compounds

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a recent study was undertaken on the purpose to analyze the already described but structurally not characterized compounds. Besides the title compounds, the phases α- and β-$Hg_2Te_2O_7$, and the hydrous tellurates(VI) $Hg_2(H_4TeO_6)$-$(H_6TeO_6)\cdot 2H_2O$ and $Hg(H_4TeO_6)$ have been prepared during this study. Results of these investigations will be published elsewhere.

This article reports on the single crystal growth, structure analyses and thermal behaviour of the new phase Hg_2TeO_5 and the well-known Hg_3TeO_6. The previously reported structure of the latter compound is dubious since the powder simulation on the basis of the given structural data [4] is not in accordance with the powder diagrams compiled in the Powder Diffraction File (PDF) and with actual measurements of single-phase material obtained during this study. Therefore a re-investigation of the crystal structure on the basis of modern single crystal diffractometer data was performed with intent to clear up the discrepancies of the reported powder and single crystal data of Hg_3TeO_6.

Experimental Section

Sample preparation

Hg_2TeO_5 was prepared under hydrothermal conditions, starting from stoichiometric amounts of $Hg(NO_3)_2\cdot H_2O$ (Merck, *p.A.*) and H_6TeO_6 (Aldrich, 99.9 %) in demineralized water, in a teflon-lined steel autoclave at 250 °C for 10 days. Besides dark-red single crystals up to 0.3 mm in length, traces of polycrystalline Hg_3TeO_6 were observed in the final product.

Single-phase polycrystalline Hg_3TeO_6 was prepared according to *Jander* and *Kienbaum* [6] by precipitation of a $Hg(NO_3)_2$ solution with a $K_2H_4TeO_6$ solution in slight excess and subsequent boiling of the obtained precipitate on a water bath for 2 h. Amber coloured single crystals of Hg_3TeO_6 with mostly plate-like habit were grown by heating a mixture of elementary Hg, HgO and TeO_3 in the molar ratio 1:1:1 and adding of small amounts of $HgCl_2$ as mineralizer in an evacuated and sealed silica glass tube at 520 °C for 5 d. TeO_3 was prepared by heating H_6TeO_6 at 400 °C for 24 h in a platinum crucible in air. Besides small droplets of elementary Hg and traces of $HgCl_2$, Hg_3TeO_6 had formed as the only crystalline product detected by XRPD.

X-ray analyses

XRPD measurements of the polycrystalline products were performed on a Philips X′Pert system (Cu-K$\alpha_{1,2}$ radiation (λ = 1.54060, 1.54439 Å), Bragg-Brentano geometry, silicon single crystal sample holder, 5-120°/ 2θ, 0.02°/ step, 10 s/ step).

The quality of single crystals of both compounds used for structure analyses was primarily checked under a polarizing microscope. Intensity data were then measured in the ω-scan mode on a SMART-CCD three-circle diffractometer. An absorption correction was applied to both data sets using the program HABITUS [7] by minimizing the internal R_i value and optimizing the crystal shape. The so derived habit was the basis for the numerical absorption correction. The crystal structures were solved by direct methods and refined with the SHELX97 program package [8]. In the final least-squares cycles for Hg_3TeO_6 all atoms were refined anisotropically, whereas in Hg_2TeO_5 only the heavy atoms Hg and Te were refined anisotropically and the O atoms isotropically. During refinement of the latter structure racemical twinning was detected; under consideration of an inversion twin a twin ratio of approximately 1:1.3 was calculated for the measured crystal. The final difference Fourier maps for both structure refinements did not indicate any additional atomic sites, and the highest difference peaks were located close to the mercury positions. Further details of data collections and structure refinements are listed in Table 1. Final atomic coordinates, isothermal displacement parameters and selected distances for both structures are given in Tables 2 and 3, respectively. Additional crystallographic information on each compound is available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, e-mail: crysdata@fiz-karlsruhe.de, by quoting the literature citation, the name of the author and the depository numbers listed at the end of Table 1. All structure representations were drawn with the program ATOMS [9].

Thermoanalytical measurements

The thermal behaviour of single-phase material of Hg_2TeO_5 and Hg_3TeO_6 was examined in an open system under a flowing N_2 atmosphere using a Mettler-Toledo DSC-25 system for DSC measurements (heating rate 5 °C·min^{-1} in the range 35-520 °C, Al crucibles) and a TG-50 system (heating rate 5 °C·min^{-1} in the range 35-700 °C, corundum crucibles) for thermogravimetrical measurements.

Results and Discussion

Both intensities and *d*-values of the strongest reflections of polycrystalline Hg_2TeO_5 are in good agreement with the XRPD data of the phase with nominal composition "$Hg_3Te_2O_9$" (PDF-entry # 39-0021). This compound is reported to occur as a dark-red crystalline product [1], similar to Hg_2TeO_5, and therefore it is most likely that the phase "$Hg_3Te_2O_9$" in fact has the composition Hg_2TeO_5. This compound can be classified as a basic mercury salt of tetraoxotellurium(VI) acid, or in older nomenclature meta-telluric acid, H_2TeO_4 [10]. Neutral salts of this acid with the formulas $M^{II}TeO_4$ (M = Ca [11], Cu [12], Sr [11, 13]) and $M^{I}{}_2TeO_4$ (M = Li [14], Na [15, 16], Cs [17]) are known for a long time, but basic salts of the type $M^{II}TeO_4\cdot M^{II}O$ (= $M^{II}{}_2TeO_5$) are restricted only to Pb_2TeO_5 [18] and Hg_2TeO_5 so far[1].

The crystal structure of Hg_2TeO_5 is made up of corner-sharing $[TeO_6]$ octahedra forming isolated infinite chains of composition $^{1}_{\infty}[TeO_{4/1}O_{2/2}]$ which extend parallel to [100] (Fig. 1). The Hg atoms are situated inbetween the chains and interconnect the chains via common oxygen atoms. The $[TeO_6]$ octahedra are slightly distorted from the ideal geometry and the Te-O bond length distribution with the longest distances to the bridging atom O3 and a mean of 1.942 Å is in the typical range for a hexa-coordinate Te

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[1] Pb_2TeO_5 and Hg_2TeO_5 crystallize in different structure types.

Table 1 Hg_2TeO_5 and Hg_3TeO_6. Crystallographic data and specifications of data collection, structure solution and refinement.

	Hg_2TeO_5	**Hg_3TeO_6**
Diffractometer	− SMART CCD system (Siemens) −	
Radiation; wavelength / Å	− Mo K$\bar{\alpha}$; 0.71073 −	
Temperature / °C	− 22(2) −	
Crystal dimensions / mm	0.09·0.04·0.03	0.12·0.12·0.08
Crystal description	dark red column	amber plate
Absorption correction	− numerical using HABITUS [7] −	
Crystal system	orthorhombic	cubic
Space group (no.)	$Pna2_1$ (# 33)	$Ia\bar{3}$ (# 206)
Formula units Z	4	16
lattice parameters		
a / Å	7.3462(16)	13.3808(6)
b / Å	5.8635(12)	
c / Å	9.969(2)	
V / Å^3	429.41(16)	2935.78(19)
Formula weight / g·mol^{-1}	608.78	825.37
μ / mm^{-1}	77.989	81.447
X-ray density / g·cm^{-3}	9.417	9.153
Range $\theta_{min}-\theta_{max}$ / °	4.03 − 30.23	4.31 − 30.44
Range h; k; l	−10→10; −8→8; −13→13	−18→17; −19→19; −18→18
Structure solution and refinement	− SHELX97 [8] −	
Measured reflections	4338	12326
Independent reflections	1261	609
Observed reflections [$I > 2\sigma(I)$]	1143	526
R_i	0.056	0.085
Coefficients of transmission T_{min}; T_{max}	0.0266; 0.2129	0.0071; 0.0691
Number of parameters	50	33
Extinction coefficient (SHELXL97)	0.00329(19)	0.00047(3)
Difference electron density / e$^-$·Å^{-3} Δ_{max}; Δ_{min}	2.28; −2.16	2.62; −1.42
with distance / Å to atom	0.89 (Hg2) 0.78 (Hg1)	0.80 (Hg) 1.09 (Hg)
$R[F^2 > 2\sigma(F^2)]$; $wR2(F^2$ all)[a]	0.0295; 0.0736	0.0221; 0.0525
Flack parameter [22]	0.440(16)	
Goof	1.067	1.111
CSD-number	391134	391133

[a] $w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$ with $P = (F_o^2 + 2F_c^2)/3$

Table 2 Hg_2TeO_5 and Hg_3TeO_6. Atomic coordinates and equivalent isotropic displacement parameters /Å^2.

Atom	Wyckoff position	x	y	z	U_{eq}[a]
Hg_2TeO_5					
Hg1	4 *a*	0.01723(8)	0.27124(8)	0.33557(4)	0.01614(16)
Hg2	4 *a*	0.23553(7)	0.27230(8)	0.67245(5)	0.01314(17)
Te	4 *a*	0.36717(13)	0.25835(11)	0.00003(18)	0.00565(17)
O1	4 *a*	0.0536(12)	0.4580(14)	0.5577(8)	0.0108(16)
O2	4 *a*	0.0874(11)	0.6546(14)	0.3203(9)	0.0131(16)
O3	4 *a*	0.1178(11)	0.1235(12)	0.0024(9)	0.0093(13)
O4	4 *a*	0.2134(11)	0.0458(16)	0.4377(9)	0.0119(16)
O5	4 *a*	0.3366(11)	0.3515(14)	0.1850(10)	0.0142(15)
Hg_3TeO_6					
Hg	48 *e*	0.37464(3)	0.20956(2)	0.03824(2)	0.01228(14)
Te1	8 *a*	1/2	0	0	0.0063(3)
Te2	8 *b*	1/4	1/4	1/4	0.0062(3)
O1	48 *e*	0.5066(5)	0.0071(4)	0.1444(5)	0.0098(13)
O2	48 *e*	0.2568(5)	0.1048(5)	0.2443(5)	0.0110(14)

[a] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}\mathbf{a_i}^*\mathbf{a_j}^*\mathbf{a_i}\cdot\mathbf{a_j}$

Table 3 Hg_2TeO_5 and Hg_3TeO_6. Selected interatomic distances /Å and angles /°.

Hg_2TeO_5								
Hg1-	O5	2.129(9)	Hg2-	O1	2.069(9)	Te-	O4	1.892(9)
	O4	2.205(9)		O2	2.083(9)		O2	1.921(9)
	O2	2.311(8)		O5	2.527(8)		O5	1.936(10)
	O1	2.485(8)		O4	2.696(9)		O1	1.942(8)
	O4	2.677(8)		O2	2.825(8)		O3	1.967(8)
	O5	2.825(9)		O3	2.877(8)		O3	1.995(8)
	O3	3.018(8)		O1	2.931(9)			<1.942>
		<2.521>			<2.573>			
			∠(O1, Hg2, O2) 165.6(3)					
Hg_3TeO_6								
Hg-	O2	2.057(6)	Te1-	O1	1.937(7)	6x		
	O1	2.065(6)	Te2-	O2	1.947(7)	6x		
	O2	2.568(6)						
	O1	2.585(6)						
	O1	2.759(6)						
	O2	2.825(7)						
		<2.477>						
∠(O2, Hg1, O1)		169.5(2)						

atom. Although both crystallographically independent Hg atoms are hepta-coordinate and have comparable mean bond lengths of d(Hg-O) ≈ 2.55 Å, they show a different crystal chemical behaviour. Hg1 has a cationic function analogous to that of Hg^{2+} in many salt-like mercury(II) oxo compounds, but unlike in most of the corresponding structures a pronounced linear [$2+x$] or [$x+2$] coordination is not realized for this atom. The Hg1-O distances range from 2.129(9)-3.018(8) Å with the longest distance to the bridging O3 atom of the $^1_\infty[TeO_{4/1}O_{2/2}]$ chain. Hg2 is the "basic" mercury atom with the characteristics of the anionic mercurate group, HgO_2^{2-} [19]. The latter features

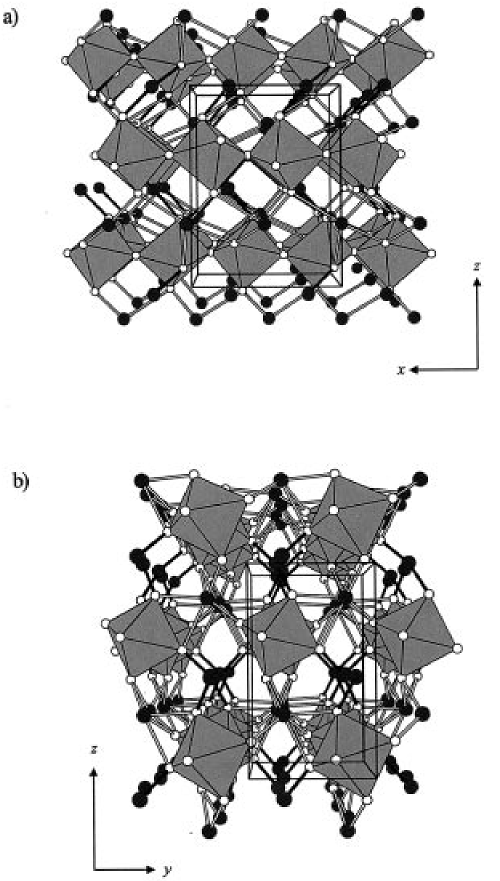

Fig. 1 Hg_2TeO_5. Projection of the crystal structure in perspective viewing along [010] (a) and along [100] (b). The [TeO_6] octahedra are plotted in polyhedral representation, the Hg atoms as dark-grey spheres. For Hg2 only short Hg-O bonds < 2.1 Å are given as solid lines; for Hg1 bonds with distances 2.1 Å < d(Hg-O) < 3.1 Å are drawn as open lines.

two very short Hg-O bonds with a mean of 2.076 Å and a roughly linear ∠(O1-Hg2-O2) angle, and bridges two adjacent Te-O chains. All O atoms in Hg_2TeO_5 show CN = 4 with a more or less distorted tetrahedral environment. The equatorial O atoms of the $^1_\infty[TeO_{4/1}O_{2/2}]$ chain have three Hg and one Te atoms as coordination partners whereas the bridging atom O3 is bonded to two Hg and two Te atoms.

XRDP analysis of ground Hg_3TeO_6 crystals showed very good agreement with the data given by *Westman* and *Magnéli* for the strongest reflections of the type $h + k + l = 2n$, indicating a body-centred cell [20] (PDF entry #11-0560). In later recorded Guinier exposures of Hg_3TeO_6 some additional weak reflections were obtained and assigned to a reduction of the symmetry from an *I*-centred Bravais lattice to a primitive cell [21] (PDF entry #14-0066). However, the reported weak reflections were not observed in the present investigation, thus demonstrating that the body-centred cell is essentially correct which is also consistent with the previously reported structural model of Hg_3TeO_6 in space group $Ia\bar{3}d$ [4]. Nevertheless, the simulated powder pattern of this model does not fit the measured data, and neither intensities nor reflection conditions are in agreement as depicted in Fig.2. For example, the reflections (114) and (334) clearly violate the reflection condition $hhl : 2h + l = 4n$ indicating a diamond glide plane *d* perpendicular to [110]. This reveals a symmetry reduction from $Ia\bar{3}d$ to $Ia\bar{3}$, and therefore the structure was solved and refined in the latter space group. The finally obtained model is in good agreement with the powder data (Fig. 2). The crystal structure of Hg_3TeO_6 is built up of a body-centred packing of [TeO_6] octahedra with the Hg atoms situated in the interstices of this arrangement. The Hg atom is surrounded by six O atoms in distorted octahedral positions and interconnects the [TeO_6] octahedra (Fig. 3). In contrast to the previous model in space group $Ia\bar{3}d$ [4] where one Te atom in position 16 *a*, one Hg in 48 *g* and one O atom in 96 *h* are reported and which leads to a nearly ideal [TeO_6] octahedron with a bond length of 1.98 Å and a slightly distorted [HgO_6] octahedron with approximately equidistant bond lengths of *d*(Hg-O) ≈ 2.33 Å, in the actual model one Hg atom and two crystallographically independent Te and O atoms, respectively, are present. Here a pronounced linear [2+4] coordination of the Hg atom with two very short axial and four longer equatorial Hg-O bonds is realized. Both O atoms are surrounded by one Te and three Hg atoms in distorted tetrahedral positions.

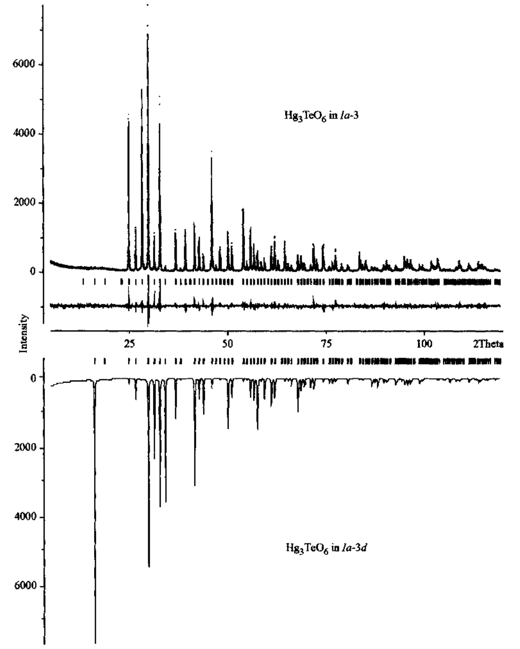

Fig. 2 Hg_3TeO_6. The Rietveld plot [23] with comparison of observed (points) and calculated profiles (solid line) and the corresponding difference pattern on the basis of the present data in $Ia\bar{3}$ (top); calculated profiles with the data of the previous model in space group $Ia\bar{3}d$ [4] (bottom).

Upon heating both title compounds decompose in an one-step mechanism into TeO_2 (detected by subsequent XRPD of the remaining solid) and the appropriate amounts of elementary mercury and oxygen (Eq. (1) and (2), Fig.

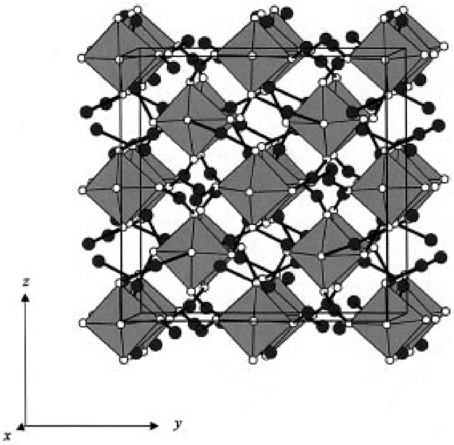

Fig. 3 Hg_3TeO_6. Crystal structure in projection approximately along [100]. The [TeO_6] octahedra are plotted in polyhedral representation, the Hg atoms as dark-grey spheres. For clarity only short Hg-O bonds < 2.1 Å are drawn.

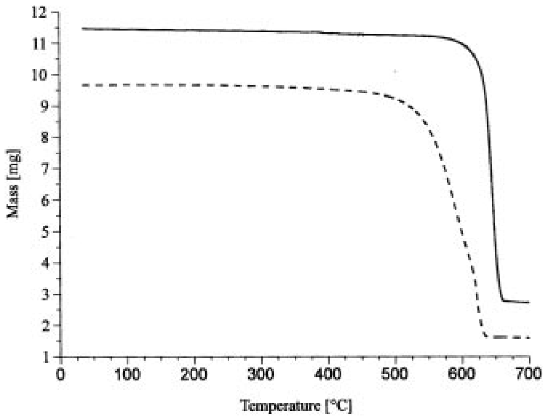

Fig. 4 TG curves of Hg_2TeO_5 (solid line) and Hg_3TeO_6 (dotted line) in the range between 35−700 °C.

4). Complementary DSC measurements did not reveal any phase transition or formation of intermediate phases. The decomposition of Hg_3TeO_6 starts at ca. 480 °C and is completed at 630 °C, whereas Hg_2TeO_5 is thermally more stable, with a decomposition range between ca. 580-670 °C.

$$Hg_3TeO_{6,s} \rightarrow 3\ Hg_{,g}\ (\uparrow) + 2\ O_{2,g}\ (\uparrow) + TeO_{2,s} \qquad (1)$$

theo. mass loss: 80.66 % (obs.: 82.1 %)

$$Hg_2TeO_{5,s} \rightarrow 2\ Hg_{,g}\ (\uparrow) + 3/2\ O_{2,g}\ (\uparrow) + TeO_{2,s} \qquad (2)$$

theo. mass loss: 73.78 % (obs.: 74.1 %)

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