Mat. Res. Bull., Vol. 20, pp. 1069-1074, 1985. Printed in the USA.
0025-5408/85 $3.00 + .00

DITELLURIUM(IV) TRIOXIDE SELENATE: A NEW SOLID PHASE IN THE SYSTEM Te-Se-O_2

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(Received June 6, 1985; Communicated by P. Hagenmuller)

ABSTRACT

$(Te_2O_3)SeO_4$ has been prepared by solving tellurium in concentrated selenic acid at 160°C. This method of synthesis is based on the corresponding for the related "ditelluryl sulphate", $(Te_2O_3)SO_4$. A crystallographic analysis carried out by the X-ray powder method shows that these compounds are isostructural (space group: $P2_1mn$, orthorhombic) and the cell parameters for the selenate are: $a = 4.807(0)$ Å, $b = 8.628(6)$ Å, and $c = 7.346(8)$ Å. The infra-red spectra of both ditelluryl derivatives can be interpretted on the basis of the proposed isomorphism. The thermal decomposition processes are also studied.

INTRODUCTION

In our previous work on the Te-Se-O_2 system we were able to identify for the first time some of the solid phases (1) corresponding to the general formula $Te_xSe_yO_{2(x+y)}$. Later on other contributions on the synthesis and characterization of several components of the same system have been published (2,3). The various phases can be described as mixed oxides of Te(IV) and Se(IV), according to indications provided by structural data now known for $Te_2Se_2O_8$ (2) and Te_3SeO_8 (4). This paper describes the synthesis, spectroscopic and structural characterization, and thermal stability of the first found compound of Te(IV) and Se(VI), corresponding to the analytical composition Te_2SeO_7.

This material is isomorphous with the so-called "telluryl sulphate", $(Te_2O_3)SO_4$, of well known crystal structure (5,6). It consists of macrocationic layers $^2_\infty|Te_2O_3|^{2+}$ composed of -Te-O- screw chains directed along the (100) plane. The layers are connected through isolated sulphate oxoanions. Thus, $(Te_2O_3)SeO_4$ could be more adequately classified as an essentially ionic oxosalt, rather than an mixed oxide as it occurs with the remaining members of this system.

EXPERIMENTAL

Ditellurium(IV) trioxide selenate was prepared by reacting elemental tellurium or sodium tellurite with 80% selenic acid as specified below:

$$Te_{(s)} + H_2SeO_4(aq) \xrightarrow[15\ h]{160°C} Te_2SeO_7(s)$$

$$Na_2TeO_{3(s)} + H_2SeO_{4(aq)} \xrightarrow[4\ h]{160°C} Te_2SeO_7(s)$$

Selenic acid was synthesized by the method described in ref.(7). The other chemicals and the reagents used for chemical analysis were supplied by Merck.

X-Ray diffraction data for the reaction products were obtained with a Siemens Kristalloflex powder diffractometer powered by a D-500 generator (W has been used as internal standard) and using Ni filtered Cu K_α radiation). The thermal analysis curves were registered with a Mettler TA 3000 apparatus and run under nitrogen flow. The I.R. absorption spectra were registered in a Perkin Elmer 1330 spectrophotometer using KBr based pellets. Finally the chemical analysis were performed following the usual procedures (8). Densities were determined by a picnometric method using CCl_4 as inmersion liquid.

RESULTS AND DISCUSSION

The reaction product obtained in both processes is a white microcrystalline solid. The chemical analysis gave the following results: Te 56.6% ; Se 17.4% ; O 26.0% (theoretical calculation for Te_2SeO_7: Te 57.2%; Se 17.7% ; O 25.1%). Oxygen content was determined by difference.

The solid density is 4.82 $g.cm^{-3}$.

The reflexions observed in the X-Ray difraction diagram were corrected with respect to the internal standard (W) and in Table 1 are gathered the corresponding spacings and relative intensities from which an orthorhombic symmetry was concluded. The refined lattice parameters and other crystallographic data are given in Table 2.

A comparison between these results and those published by Loub (5) suggest that Te_2SeO_7 synthesized by us is isostructural to $(Te_2O_3)SO_4$; which would justify to formulate it as $(Te_2O_3)SeO_4$ having also a structure consisting of $^2_\infty|Te_2O_3|$ layers parallel to the (001) plane. The layers would be joined through selenate oxoanions. This assumption seems to be further justified by the I.R. absorption spectroscopy data represented on Figure 1.

The $(Te_2O_3)SeO_4$ gives well defined absorption bands whose assignement has been made by comparison with the corresponding spectra of ditelluryl sulfate (9) and related oxocompounds of selenium and tellurium (10,11). To simplify matters we have assumed Td symmetry for both chalcogen oxoanions. Table 3 contains the assigned locations of the bands registered on both spectra between 300 and 1200 cm^{-1}

TABLE 1

X-Ray Diffraction Data for $(Te_2O_3)SeO_4$

hkl	d_{exp}	d_{calc}	I_r	hkl	d_{exp}	d_{calc}	I_r	hkl	d_{exp}	d_{calc}	I_r
001	7.371	7.347	20	220	2.100	2.100	10	005	1.470	1.469	10
011	5.610	5.594	55	132	2.049	2.049	5	214	1.439	1.439	5
020	4.324	4.314	20	221	2.019	2.019	20	105	1.405	1.405	10
110	4.208	4.199	10	202	2.015	2.012	20	322	1.390	1.390	10
101	4.028	4.022	100	212	1.960	1.959	5	224	1.382	1.382	5
021	3.724	3.720	80	141	1.902	1.901	5	251	1.377	1.377	10
111	3.649	3.646	70	004	1.837	1.837	5	153	1.354	1.354	5
121	2.943	2.942	70	222	1.823	1.823	15	243	1.342	1.343	5
102	2.921	2.919	75	014	1.797	1.796	15	125	1.336	1.336	5
022	2.799	2.797	30	231	1.790	1.789	15	035	1.309	1.308	10
112	2.766	2.765	25	133	1.738	1.738	25	234	1.301	1.301	5
031	2.681	2.678	15	104	1.715	1.716	25	054	1.258	1.258	5
130	2.469	2.468	45	024	1.689	1.690	10	006	1.224	1.224	5
003	2.450	2.449	75	051	1.681	1.680	15	045	1.214	1.215	10
122	2.417	2.417	30	232	1.648	1.648	15	225	1.203	1.204	5
013	2.356	2.356	10	150	1.623	1.624	5	170	1.194	1.194	5
201	2.286	2.284	5	240	1.605	1.605	10	145	1.177	1.177	5
032	2.267	2.265	15	223	1.593	1.594	40	324	1.163	1.163	5
103	2.183	2.182	15	301	1.565	1.565	10	235	1.149	1.149	5
040	2.158	2.157	10	034	1.548	1.548	5	431	1.096	1.096	5
023	2.131	2.130	20	152	1.486	1.485	5	226	1.058	1.058	5

TABLE 2

Refined Lattice Parameters and other Crystallographic Data for $(Te_2O_3)SeO_4$ (compared with Ditelluryl Sulphate)

$(Te_2O_3)SeO_4$	$(Te_2O_3)SO_4$
a = 4.807(0) Å	a = 4.676(2) Å
b = 8.628(6) Å	b = 8.911(3) Å
c = 7.346(8) Å	c = 6.879(4) Å
V = 304.67 $Å^3$	V = 286.63 $Å^3$
Space group $P2_1mn$	Space group $P2_1mn$
Z = 2	Z = 2
d_x = 4.85 $g.cm^{-3}$	d_x = 4.61 $g.cm^{-3}$

TABLE 3

Infrared Spectroscopic Data (in cm^{-1})

for Ditelluryl Selenate and Sulphate

$(Te_2O_3)SeO_4$	$(Te_2O_3)SO_4$	Assignment
1160 (m)*	1195 (s)	$\nu_3(EO_4)$#
1130 (m)	1055 (vs,b)	
915 (s)		
875 (s)	1000 (vs)	$\nu_1(EO_4)$
840 (vs)	965 (vs)	
795 (vs)		
	855 (sh ?)	
775 (sh)	780 (s)	$\nu_s(Te\text{-}O)$
645 (s,b)	650 (s,b)	$\nu_{as}(Te\text{-}O)$
505 (m)	505 (m)	$\nu_s(Te\text{-}O\text{-}Te)$
465 (m)	620 (m-w)	$\nu_4(EO_4)$
	460 (w)	$\nu_2(SO_4)$
430 (s)	430 (s)	δ (Te-O-Te)
370 (m)		
350 (m)		$\nu_2(SeO_4)$

*(vs = very strong; m = medium; w = weak; b = broad; sh = shoulder)

\# E = Se or S

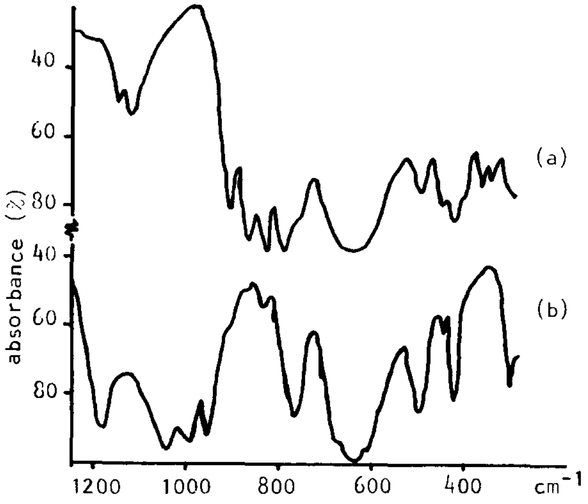

FIG. 1

Infrared Spectra of (a) $Te_2O_3SeO_4$, (b) $Te_2O_3SO_4$

These results allow confirmation of the presence in the selenate derivative of discrete SeO_4^{2-} ions though apparentely more deformed than the corresponding SO_4^{2-} in the oxosulphate. This fact is brought out by the further splitting of the ion fundamental bands.

On the other hand absorptions caused by the bond sequence Te-O--Te of the macrocationic layers $|Te_2O_3|^{2+}$ are practically identical in both spectra (figure 1). The corresponding lattice vibrations are very similar and appear in the 300-200 cm^{-1} range.

The thermal stability for both compounds has been studied, for the first time, by thermogravimetric (TG) analysis carried out under nitrogen flow (figure 2). The decomposition process of $(Te_2O_3)SeO_4$ initiates around 400°C, the first step taking place in the 400-500°C range with a weight loss of 24.7% (theoretical for SeO_2 elimination 24.9%). The second step occurs in the 510-610°C range and the weight loss registered is 3.7% (theoretical 3.6% for 0.5 mole of O_2). The former step takes place according to the complete sublimation of SeO_2:

$$Te_2SeO_7(s) \longrightarrow Te_2O_5(s) + SeO_{2(g)}$$

However the TG curve show an inflexion point around 440°C thereby suggesting that a superimposed effect is added caused by oxidation of one half of the Te(IV) to Te(VI). This process occurs with simultaneous reduction of all Se(VI) to Se(IV) which is eliminated as SeO_2. The remaining solid, Te_2O_5, could be formulated as $Te^{VI}Te^{IV}O_5$.

The latter step is bound unequivocally to the reduction of the solid to TeO_2 (12) along the following reaction:

$$Te_2O_5(s) \longrightarrow 2\ TeO_{2(s)} + {}^1/_2\ O_{2(g)}$$

Both the monoclinic Te_2O_5 isolated at 500°C in the first step and the tetragonal TeO_2 isolated at 610°C at the end of the second step were identified by X-Ray diffraction (13).

This thermal behaviour stands in sharp contrast to that of the metallic selenates in which case the reduction of the Se(VI) to the corresponding selenite occurs, and isolation of $(Te_2O_3)SeO_3$ has never been possible.

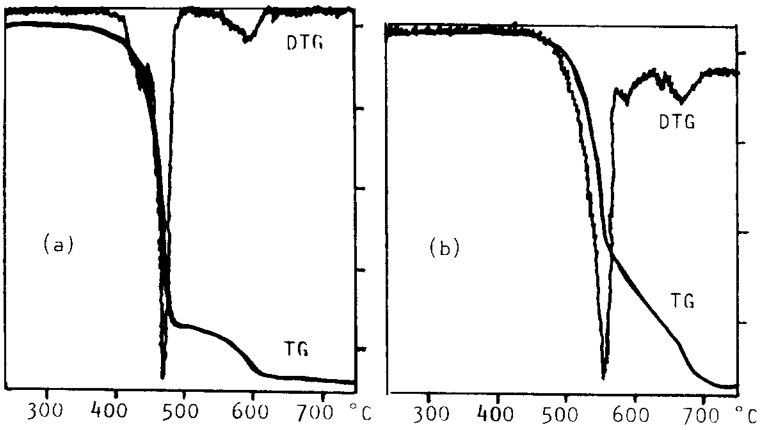

FIG. 2

Thermal decomposition of (a) $(Te_2O_3)SeO_4$, (b) $(Te_2O_3)SO_4$

On the other hand, thermal decomposition of ditelluryl sulphate (see figure 2) proceeds as a single process between 450 and 730°C with a marked inflexion around 570°C, the reaction rate remaining constant to completion. The global transformation entails the formation of TeO_2 (paratellurite) evolving SO_2 and O_2 gases whose elimination is not differentiated as it occurs with the above mentioned selenate. Furthermore, at about 510°C only X-Ray diffraction lines for TeO_2 tetragonal are registered, hence making it reasonable to exclude the isolation of crystalline Te_2O_5 at that temperature. The TeO_2 remains at the end of the process, contrary to the situation discussed above. This crystalline phase has not been mentioned before (9). These results indicate a greater thermal stability of $(Te_2O_3)SO_4$ compared to the selenate synthesized by us.

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