Preparation and Characterization of Mixed Oxides of Selenium and Tellurium

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Double oxides of Se and Te of composition Te_3SeO_8, $Te_2Se_2O_9$, and $TeSeO_4$ have been obtained for the first time by solid-state reactions between the corresponding elements and their oxides. The preparative conditions and the characterization of these compounds by thermal analysis, *X*-ray diffraction, and i.r. spectroscopy are discussed.

THERE are many references in the literature both to oxides formed from two or more metallic elements (binary oxides and complex metallic oxides) and to oxy-compounds consisting of non-metals and metals (usually formulated as oxy-salts) in which it is possible to distinguish the oxy-anion as a characteristic species in the compound. However, there are very few reports of the existence of definite oxy-compounds formed by two or more non-metallic or semi-metallic elements which might be expected to have similar characteristics to those of the previously mentioned oxides.[1]

Known examples of oxy-compounds of selenium and tellurium in which these elements are linked to other non-metallic elements by oxygen bridges, or by a covalent bond, are very rare. However, ionic interactions [2-4] (as for example, in the formation of cyclic cations of the type $[Se_4][S_4O_{13}]$ and $[Se_4][HS_2O_7]$) or covalent bonds direct to other electronegative atoms (as occurs, for example, in polythionate derivatives, such as $S_5O_6^{2-}$, which are monosubstituted by Se or Te to give [5,6] $SeS_4O_6^{2-}$ and $TeS_4O_6^{2-}$ respectively) without the intervention of the oxygen atom and with little distortion of the original structure seem to be preferred.[7,8] Only oxy-compounds of elements which have a pronounced metallic nature seem, if the metallic atom is linked to very electronegative groups, such as the halogens, to produce metal–oxygen–non-metal covalent bonds. The MX_5SeOX_5 (M = Sb or Nb; X = F or Cl) adducts in which M–O–Se bonds are formed are representative examples. A similar situation exists in other compounds such as $SbCl_5$, $POCl_3$, and $SbF_5 \cdot SO_2$.[9-11]

Thus, there has been little previous work on the existence of binary oxides formed by semi-metallic elements and, in particular, by Se and Te. This paper describes the preparation and identification of novel double oxides of these elements.

In our previous work,[12] new mixed oxides of Te with alkali metals were produced by solid-state reactions under various conditions. This method could not be applied here since the relative volatility of selenium and its oxides necessitated that these syntheses be carried out in a closed vessel under vacuum.

EXPERIMENTAL

The compound TeO_3, a yellowish amorphous solid, was obtained by complete dehydration of H_6TeO_6 (AnalaR, B.D.H.) by heating at 300 °C to constant weight.[13] The product was characterised by the usual techniques of chemical analysis [14] (Found: Te, 72.5. Calc.: Te, 72.7%). The TeO_2, Te, SeO_2, and Se were supplied by Merck.

X-Ray diffraction patterns were obtained using a Philips PW-1310 generator equipped with a chart recorder and cylindrical cameras (internal diameter 114.6 mm). Nickel-filtered Cu-K_α radiation was used.

The thermogravimetric (t.g.), differential thermogravimetric (d.t.g.), and differential scanning calorimetric (d.s.c.) curves were obtained using a Mettler TA 3000 system equipped with a TA Processor TC 10 unit and with TG 50 and DSC 20 cells.

Infrared spectra were recorded on a Perkin-Elmer 325 spectrophotometer. The samples were diluted in KBr.

RESULTS AND DISCUSSION

Table 1 lists the reaction conditions and the compositions of the products obtained. All the reactions were carried out with mixtures of finely divided reagents in a static vacuum of 10^{-3} mmHg (1 mmHg = 133.3 N m^{-2}) in sealed Pyrex or quartz ampoules. The equilibrium was frozen by immersing the ampoules in liquid nitrogen.

TABLE 1

Preparation conditions and composition of products obtained (X = unknown substance)

Reactants	θ_c/°C	*t*/h	Isolated phases
a TeO_3 + *b* Se	400	48	*a* : *b* = 3 : 2, 4 : 3, 2 : 1; Te_3SeO_8 + Se *a* : *b* = 3; Te_3SeO_8
a TeO_3 + *b* SeO_2	460	48	*a* : *b* = 8 : 9, 7 : 8, 5 : 6, 3 : 4, 2 : 3, 2 : 1, 3 : 1; $Te_2Se_2O_9$ + SeO_2 *a* : *b* = 1 : 1; $Te_2Se_2O_9$
a TeO_2 + *b* Se	500—800	72	No reaction
a Te + *b* SeO_2	500	24	*a* : *b* = 1 : 2, 1 : 1, 2 : 1; TeO_2 + X

TeO_3 + Se *Reactions*.—With molar ratios of TeO_3 : Se < 3 : 1, mixtures of excess of Se with a new solid phase were found in every case. The existence of this new phase was demonstrated by the appearance of additional reflections in the *X*-ray diffraction pattern of the reaction product. For TeO_3 : Se = 3 : 1, all the reflections corresponding to Se disappeared and identical lines to those found with TeO_3 : Se > 3 : 1 were observed, which did not correspond to any known oxide of Se or Te. The product obtained is a white microcrystalline substance which is stable in air.

Table 2 lists the analytical data of the isolated product which indicate a composition Te_3SeO_8.

TABLE 2

Chemical analysis of the mixed oxides of Se and Te

Product	Analysis (%) [a] Te	Se	O [b]
Te_3SeO_8	64.65 (64.9)	13.4 (13.4)	21.95 (21.7)
$Te_2Se_2O_9$	45.65 (45.8)	28.3 (28.35)	26.05 (25.85)
$TeSeO_4$	47.0 (47.15)	29.1 (29.2)	23.95 (23.65)

[a] Calculated values are given in parentheses. [b] Calculated by difference.

Thermal analysis of this product carried out in air at atmospheric pressure showed that it is stable up to 420 °C at which temperature decomposition begins, associated with a weight loss of 18.8%. This decomposition process is complete at *ca.* 550 °C and gives rise to tetragonal TeO_2, as the only product, which was identified by *X*-ray diffraction of the residue. This decomposition process was registered by d.s.c. as being endothermic with a reaction enthalpy of 208 J g^{-1}. Both the first derivative of the t.g. curve and the d.s.c. curve show the absence of discontinuities, which suggests that there is only one decomposition process, for which, from the d.s.c. curve, an activation enthalpy of 252.7 kJ mol^{-1} was calculated. This decomposition can be formulated as equation (1).

$$Te_3SeO_8\,(s) \longrightarrow 3\,TeO_2\,(s) + SeO_2\,(g) \qquad (1)$$

TABLE 3

Lattice spacings (Å), indexing, relative intensities, and unit-cell parameters

Te_3SeO_8 [a] $d_{expt l.}$	$d_{calc.}$	*hkl*	I/I_0	$Te_2Se_2O_9$ [b] $d_{exptl.}$	$d_{calc.}$	*hkl*	I/I_0	$TeSeO_4$ [c] $d_{exptl.}$	$d_{calc.}$	*hkl*	I/I_0
5.601	5.616	200	30	4.611	4.622	200	50	4.009	4.008	200	20
4.417	4.425	102	10	3.875	3.867	021	65	3.307	3.315	020	65
4.389	4.397	211	15	3.619	3.627	211	100	3.085	3.093	102	100
4.067	4.072	112	10	3.569	3.567	121	95	2.976	2.972	021	60
3.817	3.817	220	10	3.220	2.210	220	65	2.568	2.572	202	10
3.737	3.744	300	10	2.983	2.975	030	60	2.270	2.262	122	25
3.384	3.371	122	65	2.954	2.968	202	70	2.035	2.032	222	60
3.308	3.308	311	50	2.831	2.832	130	45	1.882	1.873	213	60
3.253	3.263	031	55	2.600	2.582	003	45	1.846	1.845	032	10
3.209	3.209	003	15	2.501	2.502	230	45	1.796	1.798	132	45
3.132	3.134	131	100	2.465	2.472	222	40	1.680	1.682	223	20
3.029	3.039	320	50	2.401	2.410	321	35	1.639	1.641	104	20
2.983	2.991	222	85	1.897	1.895	104	35	1.588	1.593	114	40
2.432	2.426	402	15	1.855	1.849	500	35	1.557	1.558	510	35
2.410	2.407	004	20	1.635	1.639	304	35				
2.401	2.393	421	20								
2.290	2.289	042	10								
2.246	2.246	500	10								
2.194	2.212	204	25								
2.038	2.036	224	10								

[a] $a = 11.23(2)$, $b = 10.40(5)$, $c = 9.62(8)$ Å. [b] $a = 9.24(4)$, $b = 8.92(6)$, $c = 7.74(5)$ Å. [c] $a = 8.01(5)$, $b = 6.63(0)$, $c = 6.70(6)$ Å.

All the observations indicate that the product is behaving as a single phase with the given stoicheiometry.

The *X*-ray diffraction pattern, obtained by the powder method, gave the spacings listed in Table 3 which were indexed in agreement with an orthorhombic symmetry for the unit cell, whose parameters are also included in the Table. Analysis of the systematic extinctions indicated the space group *P*222, *Pmmm*, or *Pmm*2.

$SeO_2 + TeO_3$ *Reactions.*—Under the conditions used, when the $SeO_2 : TeO_3$ molar ratio is greater than 9 : 8, a mixture of products is obtained. The diffraction pattern of this mixture shows, in all cases, spacings corresponding to SeO_2 together with other reflections which could not be assigned to any of the components of the original mixture.

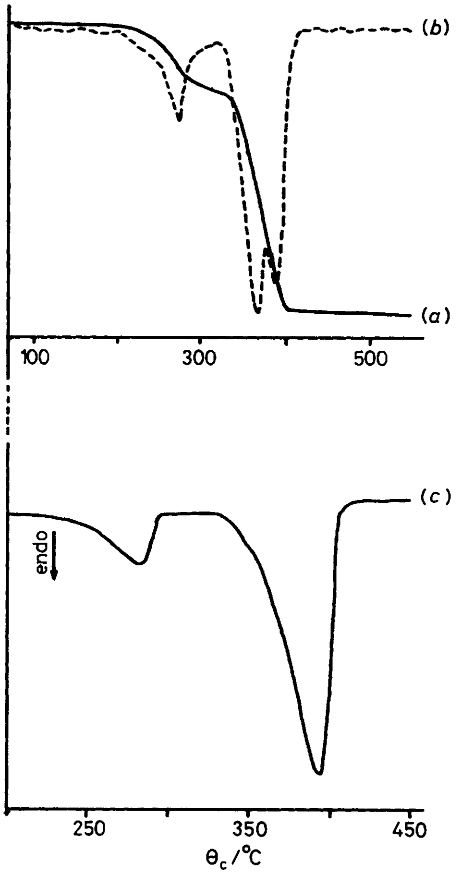
For a $SeO_2 : TeO_3$ molar ratio of 1 : 1, all the reflections assignable to SeO_2 or any other possible tellurium oxide disappear. The white microcrystalline product obtained is stable in air and has a composition of $Te_2Se_2O_9$, determined analytically as shown in Table 2.

Thermal analysis of this product (see the Figure) carried out in air shows two decomposition processes. The first, which takes place between 250 and 310 °C, is associated with a weight loss of 2.90% and, as shown by d.s.c., is endothermic with a reaction enthalpy of 69.3 J g^{-1}. Using the same reasoning as above, this process can only be formulated as equation (2) for which the

$$Te_2Se_2O_9\,(s) \longrightarrow 2\,TeSeO_4\,(s) + \tfrac{1}{2}\,O_2\,(g) \qquad (2)$$

theoretical weight loss is 2.87%, in agreement with the experimentally determined value. Kinetic analysis of the d.s.c. results gives an enthalpy of activation of 143.4 kJ mol^{-1}.

At temperatures above 322 °C, a second thermal decomposition process occurs which is complete at *ca.* 400 °C. This process is associated with a weight loss of 40.5% and differs from the previous process in that both the first derivative of the t.g. curve and the d.s.c. curve show an appreciable splitting which suggests the superposition of two simultaneous processes.[15] Separate integration of both these curves gives values of 89.5 and 286.4 J g^{-1} respectively, for the reaction enthalpies.



Thermogravimetric (*a*), d.t.g. (*b*), and d.s.c. (*c*) curves for $Te_2Se_2O_9$

Since these values are in a ratio very close to 1 : 3 and since the overall process can be formulated as equation (3)

$$TeSeO_4\ (s) \longrightarrow TeO_2\ (s) + SeO_2\ (g) \qquad (3)$$

it is suggested that there are two consecutive stages in the decomposition, equations (3a) and (3b). However,

$$4\ TeSeO_4\ (s) \longrightarrow SeO_2\ (g) + Te_4Se_3O_{14}\ (s) \qquad (3a)$$

$$Te_4Se_3O_{14}\ (s) \longrightarrow 4\ TeO_2\ (s) + 3\ SeO_2\ (g) \qquad (3b)$$

additional evidence for the formation of the assumed intermediate oxide has not been obtained. The solid residue of the process is tetragonal TeO_2 ($a = 4.810$, $c = 7.631$ Å).

The *X*-ray diffraction patterns of $Te_2Se_2O_9$ and $TeSeO_4$ have been obtained and the data are given in Table 3. Possible space groups for both compounds, *i.e.* those which correspond to the systematic extinctions, are *P*222, *Pmmm*, or *Pmm*2.

The mixed oxides, whose characteristics are described above, can be related to the Te_4O_9 and TeO_2 stoicheiometries in which the partial substitution of Te^{IV} by Se^{IV} has occurred. An attempt was made to assign the absorption bands detected in these compounds by i.r. spectroscopy. Table 4 lists the absorption bands of SeO_2 and TeO_2 together with their assignments which are in agreement with the literature.[16,17]

The $Te_2Se_2O_9$ compound gives rise to the ν(Te–O–Te) band, characteristic of TeO_3,[18] in the 835—875 cm^{-1} region. The broadening of this band is probably due to the ν(Te–O–Se) vibrations, which, owing to the presence of Se substituted for Te, would give rise to an increase in the stretching frequency.

Another band is recorded between 535 and 800 cm^{-1}. This can be assigned to the ν(Se–O) and ν(Te–O) vibrations. The appreciable overlapping between this band and the next between 400 and 500 cm^{-1} is consistent with the existence of Te–O–Se bonds in $Te_2Se_2O_9$. The i.r. spectra of selenites [19] show bands around 535—570 cm^{-1} corresponding to the δ(Se–O–Se) deformations, at a lower frequency than that found here due to the effects of possible substitution, commented on earlier. In this frequency region the δ(O–M–O) deformations for both Se and Te can also be seen.

Analogous assignments can be made for the other compound synthesised, Te_3SeO_8, whose absorption spectrum is, on the whole, more similar to that of TeO_2 with the modifications to the frequency regions indicated in Table 4.

A new double oxide, X, of selenium and tellurium has also been detected. It was formed by the reaction of Te and SeO_2 under the conditions given in Table 1 but could not be isolated since it is always formed with TeO_2. However, the presence in the *X*-ray diffraction pattern of numerous well defined lines in addition to those corresponding to TeO_2 allows the existence of this new oxide to be confirmed.

Preparation of mixed oxides of stoicheiometries $(Te,Se)O_3$, $(Te,Se)_4O_{11}$, and $(Te,Se)_2O_5$, equivalent to the corresponding tellurium oxides, has not, as yet, been

TABLE 4

Wavenumber (cm^{-1}) and assignment of the i.r. absorption bands

Te_3SeO_8	$Te_2Se_2O_9$	Assignment	TeO_2	SeO_2
925—980s	800—980vs, br	ν(Se–O)	735—850vs	760—970vs, br
	900—930 (sh)	ν(Te–O)		810—825 (sh)
		ν(Te–O–Se)		
720—820m	535—800vs, br	ν(Te–O)	425—735vs, br	560—730vs, br
780—810 (sh)	670—680 (sh)	ν(Se–O)	690—705 (sh)	690—705 (sh)
375—500s, br	400—500s, br	δ(O–M–O)	310—400s	330—380s
	410—429 (sh)	δ(Te–O–Te)		385—440s
		δ(Te–O–Se)		
250—375w, br	260—400w, br	δ(M–O–M)		285—330m
		δ(Te–O–Se)		295 (sh)

possible. However, with the exception of the first in which only Te^{VI} exists, it would appear that these phases should exist since the substitution of Te^{IV} for Se^{IV} appears to take place with relative ease.

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