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Synthesis, Crystal Structure, and Some Physico-Chemical Properties of Te_3SeO_8

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Monocrystals of a tellurium(IV) and selenium(IV) mixed oxide of composition Te_3SeO_8 have been prepared by solid state reaction between TeO_3 and SeO_2. The assignment of its IR absorption spectra has been achieved and its thermal decomposition process has been followed using TG and DSC techniques. The crystal structure of this new material has been determined by single crystal X-ray diffraction techniques: the compound has triclinic symmetry with lattice parameters: $a = 4.854(1)$ Å, $b = 6.902(2)$ Å, $c = 11.515(2)$ Å, $\alpha = 102.02(2)°$, $\beta = 100.80(1)°$, and $\gamma = 69.84(2)°$ ($R = 0.027$ for 1662 observed reflexions).

Introduction

Previous work on the Te–Se–O_2 system has been restricted to oxocompounds of Te(IV) and Se(IV), except perhaps for the recently described (*1*) "ditelluryl selenate," $(Te_2O_3)SeO_4$, which contains Se(IV) in the form of discrete oxoanions associated to layerlike macrocations $(Te_2O_3)^{2+}$. After publication of our reports on the Te–Se–O_2 system (*2–4*) tentative crystallographic data on $Te_2Se_2O_8$ (*5*) have been published together with various methods of synthesis and identification of solid phases (*6, 7*).

On the other hand, much work has been done dealing with the stereochemistry of Te(IV) due to the extraordinary "flexibility" of its coordination sphere in the oxocompounds (*8*) and the steric activity of the "lone pair" on the tellurium, localized in a strongly directional orbital (*9*) (usually described as $5s^2$ pair). In contrast to the wide range of distances and angles observed in the Te(IV)–O bonds, Se(IV) shows a clear structural regularity in both counts, deviating slightly from the expected values ($d\langle Se–O\rangle \sim 1.68 - 1.72$ Å and $\sphericalangle$ (O–Se–O) $\sim 102°$).

There are two aspects scarcely recognized in relation to the stereochemistry of both elements, Te(IV) and Se(IV). One is

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Alcock's (*10*) generic interpretation pertaining to the formation of "secondary bonding" to nonmetallic elements and the other is the existing analogy between the coordination polyhedra for Te(IV) and isoelectronic I(V) and Sb(III).

Secondary bonds are defined to exist when intramolecular distances are much larger than the normal bonds and/or other intramolecular distances that are much shorter than the van der Waals distances. Then around the central atom there usually appears a linear arrangement *Y–A–––X* of the "normal" and "secondary" bonds. For instance, in the polymorphs of TeO_2 the Te(IV) coordination polyhedron is a very deformed octahedron (*11*) (and this fact establishes its structural relation to the rutile type) defined by two axial bonds of intermediate length between the shorter two and the longer two determining the equatorial plane and arranged in position *trans* (*Y–A–––X*).

A close structural similarity may be established between the *oxo*-compounds of Te(VI) an I(VII), where it exists almost invariably as an octahedral coordination with slight variations of distances and angles. In the same manner the symmetry of Te(IV) environment may be related to isoelectronic species such as Sb(III) (*12*) and I(V) (*8*). In particular, the Te and Sb atoms cannot be distinguished in the structure of the mixed oxohalide Sb_3TeO_6Cl.

Therefore, the structural study of the oxoderivatives of these semimetals is drawing a great deal of attention today, focusing toward their descriptive and theoretical aspects along the concepts of "bond valences" of Brown (*13*) and Philippot (*9*); to that end, contribution in this area of the solid state are of special interest.

In this paper we describe the synthesis, some physicochemical and thermoanalycal properties, and the crystal structure of a new mixed oxide of Te(IV) an Se(IV), Te_3SeO_8.

Experimental

X-Ray diffraction diagrams were obtained in a D-500 Siemens apparatus of 1 kW power with Ni filtered CuK_α radiation. The IR absorption spectra were obtained with a 325 Perkin-Elmer spectrophotometer in the range 4000–200 cm^{-1}. The pelleted samples were diluted with KBr and molded under vacuum at 12,000 kg · cm^{-2}. Thermal analysis curves were obtained with a Mettler model TA 3000 thermoanalyzer equipped with a TA Processor TC-10 unit, and with TG-50 and DSC cells.

The crystal chosen for data collection was cut to a size 0.03 × 0.03 × 0.06 mm, and mounted in a computer controlled four-circle Nonius CAD 4-F diffractometer. Cell dimensions were refined by least-squares fitting of the θ values of 25 reflexions.

The telluric acid, $Te(OH)_6$, used in the preparation of tellurium trioxide and the selenium dioxide were supplied by Merck.

Results and Discussion

Synthesis and Characterization

The preparation method applied to obtain the Te(IV) and Se(IV) oxides is described below. Mixtures of TeO_3 (*14*) and SeO_2 in the molar ratio 8 : 9 are thermally treated at 460°C in an initially evacuated quartz ampoule the sample being heated for 24 hr after reaching that temperature. Subsequently the temperature was lowered stepwise 50°C at a time down to 260°C and the sample maintained for 72 hr at that temperature. Finally the equilibrium was frozen in by immersing the ampoule in liquid nitrogen. The reaction occurs according to

$$3\ TeO_{3(s)} + SeO_{2(s)} \rightarrow Te_3SeO_{8(s)} + \tfrac{3}{2}O_2.$$

An excess of SeO_2 appears necessary in order to stabilize the new oxide.

This new material is a microcrystalline white powder stable in the open atmosphere, together with some colorless mono-

TABLE I

PARAMETERS, LATTICE SPACINGS, RELATIVE INTENSITIES, AND INDEXING OF Te_3SeO_8 OBTAINED BY THE POWDER DIFFRACTION METHOD

d_{exp}(Å)	I/I_0	d_{calc}(Å)	$h\ k\ l$
5.609	100	5.589	0 0 2
3.723	19	3.726	0 0 3
3.314	33	3.318	1 0 2
3.243	34	3.238	$\bar{1}\ \bar{1}\ 3$
3.121	32	3.121	$\bar{1}\ 1\ 1$
3.023	64	3.022	0 1 3
2.794	11	2.794	0 0 4
2.429	10	2.431	$1\ \bar{1}\ 3$
2.222	34	2.221	1 3 0
1.831	19	1.832	1 1 5
1.804	19	1.804	$\bar{1}\ 0\ 6$
1.610	15	1.609	$0\ \bar{1}\ 7$

$a = 4.85(8)$ Å, $b = 6.89(9)$ Å, $c = 11.51(8)$ Å
$\alpha = 102.0(1)°$, $\beta = 100.4(7)°$, $\gamma = 69.51(1)°$

crystals. It is identified by the formula Te_3SeO_8.

The chemical analysis (*15*) of the product obtained is Te 64.6 (64.91)%, Se 13.4 (13.39)%, O 22.0 (21.70)%. The figures in parentheses are the calculated values; oxygen has been determined by difference.

Calculation of the spacing corresponding to each reflexion, relative intensities, and assigning of Miller indices given in Table I was made possible through the X-ray diffraction diagrams. It has been verified that this mixed oxide is a new phase of the Te_3SeO_8 previously isolated by us (*4*).

The lattice parameters, refined through an appropriate program (*16*) indicate triclinic symmetry; they are recorded in Table I with the other crystallographic data.

The Te_3SeO_8 IR absorption spectra show fairly well defined bands whose interpretation has been made against the corresponding spectra for related selenium and tellurium oxocompounds (*16, 17*). In the 945- to 795-cm^{-1} region there is an intense band centered around 795 cm^{-1} which could be assigned to stretching vibration (Se–O). In the 770- to 600-cm^{-1} region two very intense bands are centered around 745 and 630 cm^{-1}, respectively, with a small shoulder located at 685 cm^{-1}. Altogether these may be associated with vibration frequencies of bonds (Te–O). In addition there are three other bands which can be assigned to bond stretching. They are centered around 485, 455, and 425 cm^{-1}, and are caused by vibrations (Te–O–Te) and/or (Te–O–Se). Finally, in the region of the lowest frequencies a series of bands caused by bond deformations are present. Their assignment is as follows: a weak band centered around 395 cm^{-1} caused by flexions (O–Se–O); an intense band centered around 335 cm^{-1} assigned to a flexion (O–Te–O); an intense band, centered around 295 cm^{-1} attributed to a (O–Se–O) mode. This assignment differs from that suggested for α-$TeSeO_4$ in the low-frequency region where the 390- to 240-cm^{-1} zone would be for the (El–O–El) mode. The IR spectra are shown in Fig. 1.

The thermal analysis of Te_3SeO_8 shows it to be stable up to 400°C. The TG curve of the oxide (Fig. 2) shows an 18.7% weight loss in the 410–510°C range, which is attributed to the loss of 1 mole of SeO_2 (theoretical weight loss = 18.8%). The graph of the DSC (Fig. 2) indicates only an endothermic

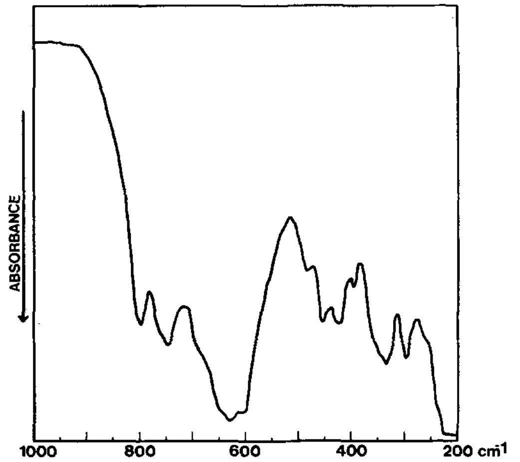

FIG. 1. The IR absorption spectra for Te_3SeO_8.

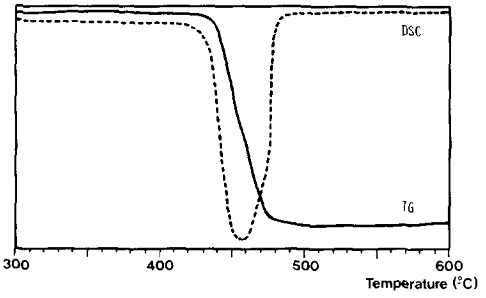

FIG. 2. TG and DSC curves for Te_3SeO_8.

effect between 420 and 550°C, corresponding to a reaction enthalpy of 208 J · g^{-1}. An examination of the X-ray diffraction diagram of residues from both processes indicates they are composed of TeO_2 (paratellurite). With this information this transformation could be interpreted as the decomposition of the initial oxide, the selenium being eliminated as SeO_2 gas under the conditions of decomposition. The process may be formulated as

$$Te_3SeO_8 \rightarrow 3\ TeO_2 + SeO_2.$$

The kinetic analysis (*18*) results obtained from DSC yield an activation energy of 251.1 kJ · $mole^{-1}$ (*19*).

Structural Analysis

Data collection. The intensities of 2208 reflections within $2 \leqq \theta \leqq 27°$ were collected at 295 K with monochromatic Mo $K\alpha$ ($\lambda = 0.7169$ Å) radiation and an $\omega/2\theta$ scan technique. The intensities were corrected for Lorentz and polarization effects, and 1662 of these were considered as in accord with the criterion $I \geqq 2\ \sigma(I)$. Two reflections were monitored periodically during the data collection and showed no crystal decomposition.

TABLE II

CRYSTAL DATA FOR Te_3SeO_8 TRICLINIC

$a = 4.854(1)$ Å
$b = 6.902(2)$
$c = 11.515(2)$
$\alpha = 102.02(2)°$
$\beta = 100.80(1)$
$\gamma = 69.84(2)$

$U = 351.4(2)$ Å^3
$Z = 2$
$M_r = 589.8$
$D_c = 5.574$ g · cm^{-3}
Space group: $P\bar{1}$

$F(000) = 508$
$\mu(MoK_\alpha) = 17.552\ mm^{-1}$
$T = 295$ K
$R = 0.027$ for 1662 observed reflexions

TABLE III

ATOMIC PARAMETERS FOR Te_3SeO_8 COORDINATES AND THERMAL PARAMETERS AS UEQ = ($\frac{1}{3}$)

Atom	*X/A*	*Y/B*	*Z/C*	UEQ
Te_1	0.85619(11)	0.13327(8)	0.30347(4)	81(1)
Te_2	0.10732(11)	0.46100(8)	0.19217(4)	80(1)
Te_3	0.48783(12)	0.74175(8)	0.42561(5)	109(2)
Se	0.35118(17)	0.82542(12)	0.09127(7)	85(2)
O1	0.25564(129)	0.02322(89)	0.43257(57)	148(19)
O2	0.01969(130)	0.35212(88)	0.32735(50)	107(18)
O3	0.15705(121)	0.67711(89)	0.31960(48)	92(17)
O4	0.08057(156)	0.04930(102)	0.14056(60)	205(22)
O5	0.65098(131)	0.30900(91)	0.44532(51)	122(18)
O6	0.58480(145)	0.77677(114)	0.21661(59)	210(23)
O7	0.17890(151)	0.64196(99)	0.07014(55)	168(21)
O8	0.51464(130)	0.30389(105)	0.19715(55)	169(20)

Scattering factors for neutral atoms and the anomalous dispersion corrections for tellurium and selenium atoms were taken from the "International Tables for X-Ray Crystallography" (*20*). The centrosymmetric group $P\bar{1}$ was obtained in the course of the structure solution. The crystal data are shown in Table II.

Structure determination. The Te and Se atoms were located from the three-dimensional Patterson map. The positions of the oxygen atoms were obtained from Fourier synthesis.

An empirical absorption correction (*21*) was applied at the end of the isotropic refinement procedure. Anisotropic full matrix least-squares refinement with units weights lead to $R = 0.027$. No trend in ΔF vs F_0 or sin θ/λ was observed. Maximum and average shift/error were 0.02 and 0.005, respectively. A final difference synthesis shows an electron density of 3 e$Å^{-3}$ located in the heavy atom positions. Most calculations were carried out with X-Ray 80 (*22*).

Table III contains the atomic coordinates and Ueq factors. The most meaningful dis-

TABLE IV

BOND LENGTHS (Å) AND ANGLES (°) FOR Te_3SeO_8

Te 1–O1$^{(1)}$	2.218(6)	Te 3–O1$^{(3)}$	2.525(6)
–O2$^{(1)}$	1.887(7)	–O1$^{(4)}$	1.874(6)
–O4$^{(1)}$	2.218(8)	–O3	1.949(5)
–O5	2.021(6)	–O5	2.861(6)
–O8	2.032(6)	–O5$^{(3)}$	1.882(7)
Te 2–O2	2.031(7)	–O6	2.611(7)
–O3	1.908(5)	Se –O4$^{(4)}$	1.718(6)
–O4	2.823(8)	–O6	1.677(6)
–O6$^{(2)}$	2.732(6)	–O7	1.700(8)
–O7	2.207(8)		
–O8	1.896(6)		
O1$^{(1)}$ – Te 1–O2$^{(1)}$	78.2(2)	O6$^{(2)}$ – Te 2–O7	85.3(2)
– –O4$^{(1)}$	97.6(2)	– –O8	163.6(3)
– –O5	87.3(2)	O7 – –O8	87.8(3)
– –O8	165.3(3)	O1$^{(3)}$ – Te 3–O1$^{(4)}$	68.7(2)
O2$^{(1)}$ – –O4$^{(1)}$	80.0(3)	– –O3	155.1(2)
– –O5	82.0(3)	– –O5	120.7(2)
– –O8	87.5(3)	– –O6	102.6(3)
O4$^{(1)}$ – –O5	160.0(3)	– –O5$^{(3)}$	90.4(3)
– –O8	82.8(3)	O3 – –O5	81.5(2)
O5 – –O8	87.6(2)	– –O6	77.6(3)
O2 – Te 2–O3	81.5(3)	– –O5$^{(3)}$	89.0(3)
– –O4	63.8(2)	O5 – –O6	109.4(2)
– –O6$^{(2)}$	86.7(2)	– –O5$^{(3)}$	65.9(2)
– –O7	168.1(2)	O1$^{(4)}$ – –O3	86.7(3)
– –O8	97.5(3)	– –O5	158.7(3)
O3 – –O4	143.5(3)	– –O6	85.0(3)
– –O6$^{(2)}$	69.1(2)	– –O5$^{(3)}$	96.3(3)
– –O7	87.4(3)	O6 – –O5$^{(3)}$	166.5(2)
– –O8	95.8(3)	O4$^{(4)}$ –Se –O6	102.5(3)
O4 – –O6$^{(2)}$	116.9(2)	– –O7	102.1(4)
– –O7	127.9(2)	O6 – –O7	102.8(4)
– –O8	79.0(3)		

Note. (1) 1 + x, y, z; (2) 1 − x, y, z; (3) 1 − x, 1 − y, 1 − z; (4) x, 1 + y, z.

tances and angles found for the Te_3SeO_8 oxide are summarized in Table IV.[1]

Structure Description

Figure 3 represents a perspective view of the unit cell along the *bc* direction. Note the alternating sequence of tellurium and oxygen atoms occurring as a type of 12-member folded heterocycle. The Te(2) end atoms are connected to the Se atoms; the latter and the remaining atoms are centrosymmetrically related. Each Te atom in the unit cell is connected to two others with a different label along the pseudocycle through the bridging oxygens.

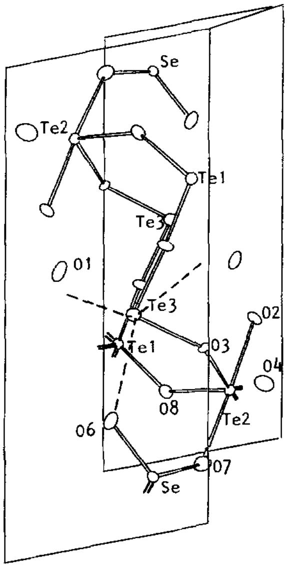

FIG. 3. A view of the unit cell along the *bc* direction in Te_3SeO_8.

Figure 4 shows the coordination environments of the tellurium and selenium atoms. The labeling of the three Te present in the

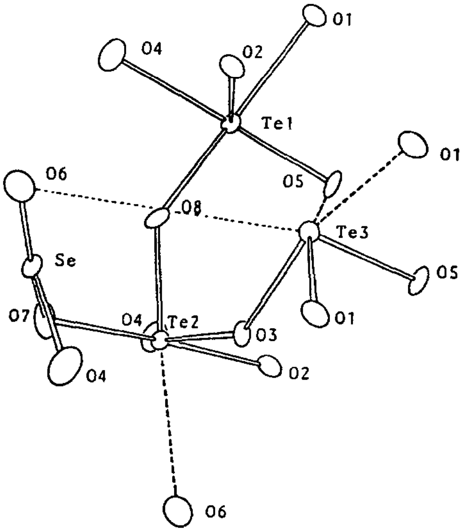

FIG. 4. Coordination polyhedra of heavy atoms (Te and Se) in Te_3SeO_8.

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[1] Supplementary data available: A list of observed and calculated structure factors and thermal parameters are also available from the Editor.

asymmetric unit, which are not equivalent, is as indicated in Fig. 3. The bond distances found for tetracoordinated Te^{IV} in TeO_2 (up to ca. 2.2 Å for the four shortest Te–O bonds (*11*) are taken as a reference. There is 4-coordination of Te in TeO_2, the closest neighbors being arranged at four of the vertices of a trigonal bipyramid (*23*).

One could accept that Te(1) is coordinated to five oxygen atoms located approximately at the vertices of square base pyramid. It is likely that this symmetry is similar to that found for $Te_2Se_2O_8$ (*5*). A relation could be established between this coordination polyhedron and an octahedron such that the Te^{IV} lone pair points to the sixth vertex, thus completing the octahedral coordination. The bond distances fall in the range of 1.887 to 2.218 Å (Table IV). The next neighboring oxygen atom is at 3.020 Å, which is approximately at the upper limit for the tellurium–oxygen covalent bond distance.

The Te(2) is linked to four neighbors oxygen atoms at bond distances within the range of 1.896 to 2.207 Å. One also encounters interaction between two other oxygen atoms placed at distances of 2.732 and 2.823 Å, rendering this tellurium coordination 4 + 2.

With this criterium the coordination number for Te(3) would be 3 + 3 since the three nearest oxygen atoms exist at bond distances within the range 1.861 to 1.949 Å but the three others farther apart are within a range of 2.525–2.861 Å range.

According to the foregoing considerations, we may consider the coordination polyhedra of the three tellurium atoms as greatly deformed octahedra, all of them sharing sides and corners, and the whole forming a 3-D structure.

The selenium of the SeO_3 group is linked to the three oxygen atoms in a pyramidal arrangement, and the sum total of the three O–Se–O angles is 307°. The differences among the three Se–O distances are not meaningful in light of the standard deviations. Two of these oxygen atoms, O(6) and O(7) respectively, are shared with the coordination polyhedra corresponding to the Te(2) and Te(3) in the same asymmetric unit, and the third, O(4), belongs to the environment of a Te(1), located in a neighboring asymmetric unit. The Se atoms environment is different in that the one that has crystalline SeO_2, in which Se is joined to 3 oxygens, form infinite chains in which the bond distances Se–O are of length 1.78 and 1.73 Å (*23*).

Using Brown's (*13*) "bond valences" criteria (*S*) through the expression corrected by Philippot (*9*)

$$S = 1.333\ (R/1.854)^{-5.2}$$

for the Te^{IV}–O bonds, it is possible to obtain a relation between the experimental bond distances and their respectives bond valences; they are inversely related. On the other hand the sum of the bond valences of each Te–O bond should equal the oxidation number of the central atom (*24*), that is, four, in our case.

Consequently, the coordination polyhedra of the Te atoms are defined by a component due to *short* bonds (1.88–2.21 Å range); another due to weaker and correspondingly *longer* bonds (up to 3.02 Å) that would complete a pseudo-octahedral coordination. The upper limit 3.1 Å (equivalent to bond valance 0.09) for Te–O bond distance

TABLE V

AVERAGE BOND DISTANCES (Å) AND BOND VALENCES FOR THE LINKS Te^{IV}–O IN Te_3SeO_8

	d(Te–O)			
Atom	Short coordn.	6-coordn.	S_{short}	$S_{6\text{-coordn.}}$
Te(1)	2.075	2.233	3.93	4.04
Te(2)	2.010	2.268	3.72	4.04
Te(3)	1.905	2.284	3.49	4.10

is a reasonable assumption generally accepted, since beyond that distance the interactions would be negligible.

Table V contains average bond distances for unequivocally covalent links (d ⟨Te–O⟩ for *short* coordination) and for weaker interactions worthy of consideration, judging by the expressed criterion (d ⟨Te–O⟩ for 6-coordination). The values of the corresponding bond valences (S_{short} and $S_{\text{6-coord.}}$) are also shown in Table V.

All these data suggest that hexa-coordination for the three Te atoms is compatible with the bond valence criterion, even though the value for Te(3) is $S = 3.98$ if only the five shorter bond distances are considered (in the 1.880–2.162 Å range).

In all cases the average d ⟨Te–O⟩ values obtained for the pseudo-octahedral coordination are of the same order as found in other binary and mixed oxides of Te^{IV} (for instance, 2.296 A for α-TeO_2 itself).

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