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The Crystal Structure of Tetragonal Selenium Trioxide

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The crystal structure of selenium trioxide has been determined by three-dimensional Fourier synthesis followed by least-squares refinement. The tetragonal unit cell ($P\bar{4}2_1c$, $a=b=9\cdot636$, $c=5\cdot28$ Å) contains two $(SeO_3)_4$ ring molecules, situated at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, their $\bar{4}$ axes coinciding with those of the cell. The average Se–O distances are 1·77 and 1·55 Å from Se to bridging and non-bridging O.

Introduction

Lehmann & Krueger (1952) described a method for the preparation of selenium trioxide in gram quantities by the action of sulphur trioxide on potassium selenate. A liquid mixture of sulphur trioxide and selenium trioxide results. Pure selenium trioxide can be obtained by distilling off the much more volatile sulphur compound. Thermal analysis of the SeO_3–SO_3 system (Mijlhoff & Gerding, 1963) revealed that mixed crystals are formed having a composition between 25 and 100 mole % SeO_3. An X-ray analysis was carried out in order to determine the constitution of the solid selenium trioxide and of the mixed crystals.

Experimental

Mixed crystals were obtained by slow crystallization from a liquid mixture, and pure selenium trioxide crystals by slow sublimation in high vacuum. The oxides are very hygroscopic and chemically active, but is was possible to select suitable crystals from a sample immersed in a commercial liquid Freon. Unit-cell dimensions were estimated from Weissenberg photographs containing aluminum powder calibration lines. Systematic absences determined the space group uniquely. Crystal data are collected in Table 1. The mixed crystal consisted of two fragments differing slightly in cell volume, probably because they had different sulphur trioxide contents.

Table 1. *Crystal data*

SeO_3 crystal	$a=b=9\cdot636\pm0\cdot0003$, $c=5\cdot28\pm0\cdot02$ Å.
SeO_3–SO_3 mixed crystal	$a=b=9\cdot486-9\cdot413$, $c\simeq5\cdot12$ Å.

Space group: $P\bar{4}2_1c$

Intensities were obtained from integrated equi-inclination Weissenberg photographs made with Cu $K\alpha$ radiation by the multiple film technique, the crystal rotating about the c (needle) axis. The zero to fourth level intensities for the pure selenium trioxide crystal were scaled by comparison with $h0l$ intensities derived from a precession photograph made with Mo $K\alpha$

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radiation. Since the crystals were lost before their shape could be determined, no corrections for absorption were made.

Two-dimensional synthesis

The cell volume and symmetry indicated the presence of eight SeO_3 units in general positions, arranged in two groups of four around the two $\bar{4}$ axes (Fig. 3). This was confirmed by the Patterson synthesis of the visually estimated mixed crystal $hk0$ intensity data, which were the first available. The vector OP in Fig. 1 corresponds to the Se–Se diagonal in the projection of the ring along (001). Fig. 2 represents the minimum function corresponding to two Patterson functions related by a translation OP. Here the two tetrameric rings at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ show up clearly. Since the mixed-crystal intensities could not be determined unambiguously because of the partial overlap of the reflexions associated with the two fragments, no further refinement of these data was carried out.

The photometered $hk0$ intensities from the pure selenium trioxide were used for further corrections of the x, y parameters by means of the centrosymmetric electron-density projection along the c axis, starting from the positions found for the mixed crystal. After all the structure factors had the right sign, individual temperature factors were computed and a final adjustment was made on the basis of a difference Fourier synthesis.

The estimation of the individual temperature factors was carried out as follows: If F_1 and F_2 are the contributions of two different kinds of atom to the structure factor and K is the scaling factor, then $KF_{\rm obs} = F_1\exp(-B_1s^2)+F_2\exp(-B_2s^2)$. The exponentials were computed by least-squares methods as coefficients of F_1 in small s^2 intervals, and a plot of the logarithms of both these coefficients *vs* s^2 gives K, B_1, and B_2.

Three-dimensional synthesis and refinement

From the x, y coordinates and the Se–O distances found from electron diffraction in the gas phase, of 1·56 and 1·80 Å for Se to non-bridging and bridging O (Mijlhoff, 1965), a unique model could be constructed that did not violate the common notions about valence angles. The first set of z parameters was derived from this model; the two $(SeO_3)_4$ molecules were placed in the cell with their centres at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. A three-dimensional Fourier synthesis of the electron density was computed and the coordinates corrected with the suggested shifts, multiplied by a factor 1·7 to account for the fact that the projection along [001] is centrosymmetric (*cf.* Cruickshank, 1950; Shoemaker, Donohue, Schomaker & Corey, 1950). Further refinement was accomplished by means of difference syntheses, leaving out reflexions with very large discrepancies between $F_{\rm obs}$ and $F_{\rm calc}$, *i.e.* ΔA or $\Delta B > 10$ (Table 4). Table 4 shows that the $F_{\rm obs}$ of a number of high intensity, low angle reflexions were systematically too low, probably because no extinction corrections were made. For most other reflexions there was much better agreement. It was found necessary, with isotropic temperature factors, to readjust the scaling factors for the individual layer lines by about 10% or less.

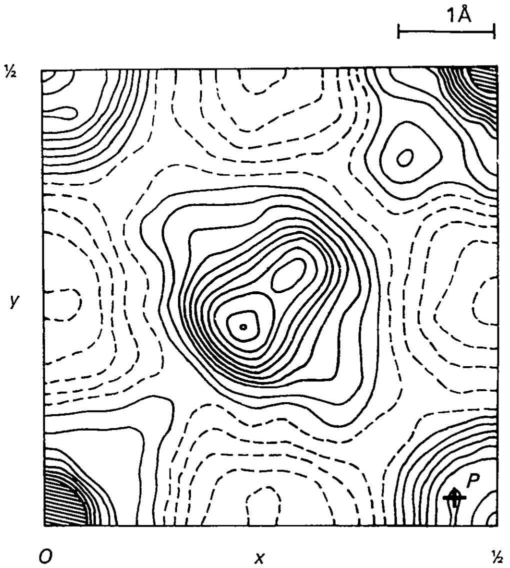

Fig. 1. Patterson projection along [001] of $\frac{1}{4}$ of the unit cell, arbitrary scale. P is the end point of a diagonally opposed Se–Se distance vector.

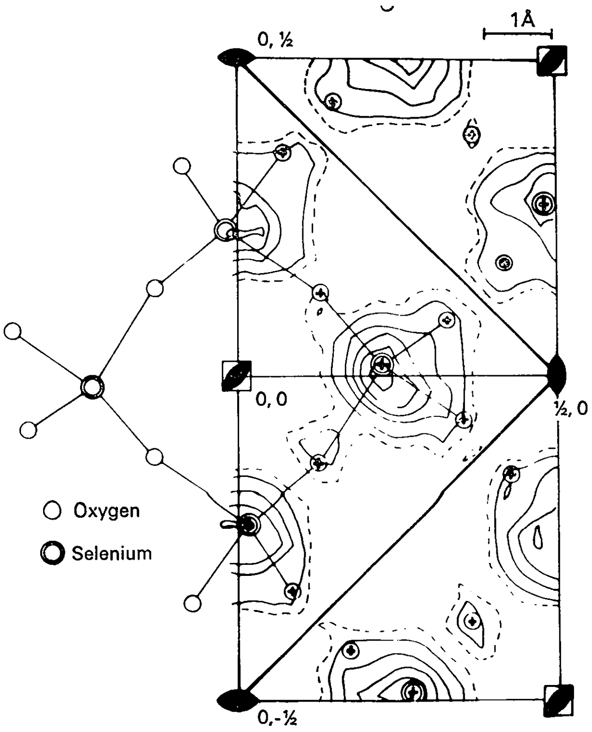

Fig. 2. Minimum function on arbitrary scale. The shift was made along OP in Fig. 1. Circles mark initial choice of atomic positions.

Table 2. *Final atomic positions and isotropic temperature factors for the asymmetric unit*

	x	y	z	B
Se	0·224	0·013	0·063	1·92
O(1)	0·120	0·101	−0·156	2·25
O(2)	0·336	−0·055	−0·104	2·6
O(3)	0·234	0·100	0·309	2·6

Further refinement was carried out with a least-squares program for refinement of coordinates and isotropic individual temperature factors, written by Rutten (1963) for the EL X1 computer. Again, the structure factors of Table 4 were left out of consideration. After three cycles the shifts were less than the corresponding standard deviations and R had decreased

Table 3. *List of structure factors used for refinement*

h	k	l	F_{calc}	F_{obs}	h	k	l	F_{calc}	F_{obs}	h	k	l	F_{calc}	F_{obs}
0	2	0	2.4	2.4	5	5	0	51.0	51.4	2	8	1	14.2	13.4
	8		34.9	33.6		8		15.1	15.9		9		10.2	10.7
	10		16.0	15.0		9		25.2	27.1		10		8.1	7.6
1	1	0	25.3	24.3		11		4.7	4.5		11		22.5	23.5
	2		9.3	8.2		12		9.9	11.0		12		4.7	4.3
	3		19.1	17.9	6	6	0	22.6	23.8	3	4	1	19.6	20.2
	4		21.0	18.4		7		15.4	14.6		5		24.7	24.5
	5		25.6	23.1		8		10.6	10.1		6		29.3	29.9
	6		6.7	6.4		9		11.5	11.9		7		11.6	11.7
	7		26.3	27.7		10		6.8	8.0		8		8.0	6.4
	8		11.7	12.3	7	7	0	30.7	31.8		9		15.1	15.5
	9		36.0	37.4		8		5.4	6.0		10		7.9	5.7
	10		11.8	12.0		10		8.0	7.0		11		12.7	13.2
	11		14.4	17.1		11		14.6	15.9	4	5	1	53.1	54.8
	12		15.5	17.4	8	8	0	9.6	10.5		6		17.3	16.9
	13		9.0	10.8		9		6.9	6.0		7		4.6	5.7
2	3	0	32.4	31.0	0	3	1	32.2	31.0		8		6.2	6.0
	4		3.5	3.5		4		17.6	17.0		9		28.0	30.1
	6		42.5	39.7		6		29.1	26.5		10		11.6	11.8
	7		15.3	13.8		7		5.0	5.8		11		7.9	8.2
	8		12.6	12.4		8		6.9	8.1	5	6	1	5.3	5.9
	10		14.0	11.9		9		39.8	39.6		7		20.2	21.1
	12		11.9	13.7		10		7.7	6.6		8		17.1	17.9
3	3	0	29.0	26.3		11		6.2	8.0		9		8.7	10.0
	5		14.7	15.6		12		4.3	5.1		10		9.9	9.2
	6		16.3	16.0	1	3	1	18.7	17.0		11		8.4	9.2
	7		42.9	43.7		5		15.0	13.4	6	7	1	28.9	29.2
	8		7.8	7.6		6		15.3	15.4		8		17.5	17.8
	9		9.6	11.6		7		20.4	19.5		9		5.7	6.5
	10		17.5	19.8		8		11.8	12.8		10		4.8	5.9
	11		21.8	23.1		9		15.8	15.5	7	8	1	8.9	9.2
4	4	0	58.9	58.6		10		7.4	6.9		9		12.2	12.5
	5		26.9	26.8		11		11.9	12.1	8	9	1	12.8	14.5
	6		12.3	11.1		12		4.4	4.8	0	1	2	8.5	9.0
	8		17.8	19.7	2	4	1	33.8	36.2		2		5.5	6.2
	9		10.5	10.5		5		12.5	11.1		5		9.3	9.7
	10		12.6	12.3		6		6.4	7.3		6		16.6	15.8
	11		8.8	9.4		7		49.0	48.7		7		40.0	38.9

Table 3 (*cont.*)

h	k	l	F_{calc}	F_{obs}	h	k	l	F_{calc}	F_{obs}	h	k	l	F_{calc}	F_{obs}
0	8	2	13.3	14.3	4	11	2	15.0	12.6	3	5	3	32.7	32.5
	10		8.0	7.1	5	5	2	26.6	26.9		6		10.9	11.3
	11		15.0	15.7		6		21.4	23.8		7		11.2	11.2
1	0	2	5.8	7.5		8		11.6	13.6		8		15.4	15.6
	2		29.9	29.6		9		20.5	20.2		9		18.8	18.4
	3		5.3	3.8		10		5.7	5.1	4	6	3	29.3	28.4
	4		19.1	19.0	6	6	2	22.8	24.0		9		13.6	15.3
	5		28.5	29.1		7		12.1	11.8	5	6	3	11.8	12.6
	6		21.3	21.8		9		14.9	14.7		7		26.5	29.6
	7		26.0	25.9		10		12.1	13.0	6	7	3	8.1	7.8
	8		13.3	12.2	7	7	2	21.8	21.6		8		9.5	8.8
	9		18.8	18.7		8		12.5	11.6		9		8.5	7.3
	10		9.5	8.9	8	8	2	14.4	12.3	7	8	3	11.8	10.8
	11		10.4	7.5	0	3	3	6.8	7.5	0	0	4	14.4	14.2
2	3	2	9.4	10.6		4		5.4	7.8		1		26.5	28.4
	4		10.4	10.2		5		25.2	26.5		3		43.1	44.5
	5		46.9	48.3		6		42.4	41.7		7		34.2	33.4
	6		32.5	33.9		8		13.5	13.3	1	1	4	13.6	11.1
	8		9.4	8.2		9		10.6	9.2		3		10.5	11.2
	9		23.3	23.2		10		8.0	7.4		4		19.9	19.9
	10		6.9	6.6	1	2	3	15.8	15.3		5		12.9	12.6
3	3	2	28.4	28.9		3		29.8	30.3		6		17.4	17.7
	4		37.5	38.2		4		26.2	25.9		9		10.3	8.9
	5		9.1	9.7		5		18.1	18.2	2	2	4	7.4	9.2
	6		15.1	16.5		6		18.1	18.5		3		9.5	10.0
	7		25.6	26.7		7		22.0	22.3		5		36.1	36.4
	8		11.7	11.3		8		11.9	10.7		9		26.3	21.8
	9		13.4	13.3		9		14.3	15.9	3	3	4	13.9	12.5
	10		9.1	9.6		10		11.0	9.6		4		29.6	28.1
	11		14.8	12.8	2	3	3	17.9	17.1		7		12.1	12.1
4	4	2	38.6	39.6	2	4	3	53.8	53.4		8		9.2	7.5
	5		10.4	11.7		6		8.1	6.5	4	7	4	26.3	22.3
	7		25.5	26.7		7		15.5	15.8		8		11.0	8.2
	8		19.0	19.3		8		20.9	19.4	5	6	4	19.2	10.4
	9		8.0	8.1		10		11.5	10.1	6	6	4	13.8	11.2
	10		6.4	5.9	3	4	3	8.1	9.4					

Table 4. *List of structure factors not used in refinement* ($R=20\%$)

h	k	l	F_{calc}	F_{obs}	h	k	l	F_{calc}	F_{obs}	h	k	l	F_{calc}	F_{obs}
0	4	0	63·2	52·5	1	2	1	43·1	35·4	0	4	2	53·6	50·7
2	2	0	121·2	77·1			4	28·1	22·9	2	2	2	61·2	51·4
0	1	1	77·5	51·1	2	3	1	64·8	55·9	0	1	3	11·0	6·0
		2	46·0	37·6	0	0	2	51·9	45·9			2	58·4	39·2
		5	54·9	45·2			3	48·5	44·9	1	2	4	37·2	30·3

Table 5. *Atomic positions* (Å) *and isotropic temperature factors, with standard deviations*

	x	σ_x	y	σ_y	z	σ_z	B	σ_B
Se	+2·1556	0·0014	+0·1209	0·0013	+0·3329	0·0020	1·93	0·02
O(1)	+1·151	0·011	+0·971	0·011	−0·823	0·015	2·25	0·20
O(2)	+3·239	0·011	−0·528	0·011	−0·550	0·014	2·60	0·21
O(3)	+2·341	0·011	+0·959	0·011	+1·633	0·015	2·60	0·21

Table 6. *Interatomic distances and angles and their standard deviations in* $(SeO_3)_4$

The numbers refer to Fig. 3.

Distances				Angles			
Se–O		O–O		O–Se–O		Se–O–Se	
$\sigma=0·013$ Å		$\sigma=0·018$ Å		$\sigma=0·85°$		$\sigma=0·75°$	
1–5	1·75 Å	5–8	2·68 Å	5–1–8	98·7°	1–5–2	123·2°
1–8	1·80	9–13	2·79	9–1–13	128·2		
1–9	1·54	8–9	2·72	8–1–9	108·4		
1–13	1·56	5–13	2·73	5–1–13	110·5		
		5–9	2·59	5–1–9	103·2		
		8–13	2·64	8–1–13	103·2		

to 6%. The resulting parameters are collected in Table 2. Table 3 lists the final calculated structure factors together with the observed *F*'s. Since absorption has been neglected the *B* values include some absorption effects and therefore probably only their differences are more or less significant.

Discussion of the structure

The arrangement of the molecules in the cell is given in Fig. 3. The molecule itself resembles closely the $(PNCl_2)_4$ molecule, described by Ketelaar & de Vries (1939) and reinvestigated recently by Hazekamp, Migchelsen & Vos (1962).

The final coordinates and isotropic temperature factors, together with their standard deviations, are given in Table 5, and the intramolecular distances and angles in Table 6. The numbering in Table 6 corresponds to Fig. 3.

The Se–O distances in the ring are not equal, and in view of the standard deviations the difference must be regarded as significant (significance level 1%). The non-bridging Se–O distances are considerably shorter. This is a common feature within the class of polyoxo complexes in which a number of AO_4 tetrahedra share oxygen atoms.

The differences in bridging and non-bridging bond lengths can be explained in terms of $d_\pi - p_\pi$ bonding, which has been shown (Craig, MacColl, Nyholm, Orgel & Sutton, 1954; Jaffé, 1954; Stone & Seyferth, 1955; Cruickshank, 1961) to occur in these tetrahedrally coordinated oxo complexes.

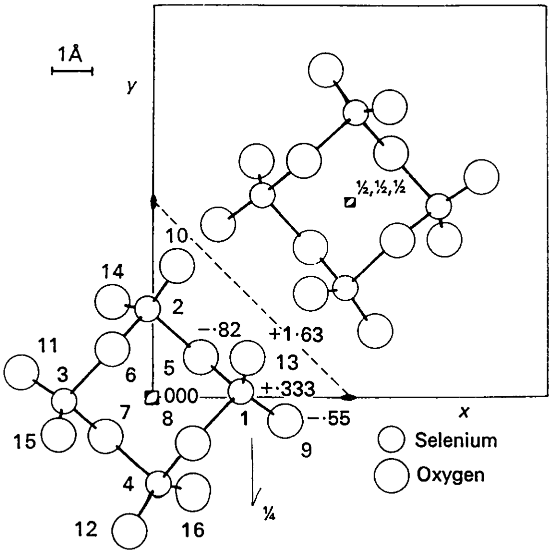

Fig. 3. Positions of $(SeO_3)_4$ molecules in the unit cell. *z*-coordinates in asymmetric unit are in Å.

Cruickshank (1961) has reviewed most known distances in this type of compound; recently data about $P_4O_{12}^{4-}$ in $Na_4P_4O_{12} . 4H_2O$ and S_3O_9 were given by Ondik (1963) and Pascard & Pascard-Billy (1963) respectively. Following Cruickshank's reasoning there are two systems of π orbitals in the Se_4O_{12} molecule. One extends throughout the molecule and includes *p* orbitals of both kinds of oxygen atom and one d_γ orbital of the Se atom, the mismatch of *p* orbitals on the bridge-oxygen being only slight. In the other $p_\pi - d_\pi$ orbitals only the non-bridging oxygen *p* orbitals are involved, together with the other selenium d_γ orbital. The π bond orders are $41/186 = 0{\cdot}22$ and $52/186 + \frac{1}{2} = 0{\cdot}78$ for the bridging and non bridging Se–O bonds respectively.

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