

## The crystal structure of SeO<sub>2</sub> at 139 and 286 K

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### SeO<sub>2</sub> / *X-ray crystal structure*

**Abstract.** The structural model of tetragonal SeO<sub>2</sub> proposed by McCullough [JACS **59** (1937) 789] has been refined at 139 and 286 K. Space group  $P4_2/mbc$ ,  $Z = 8$ ,  $M_w = 110.96$ ,  $a = 8.3218(9)$ ,  $c = 5.0541(6)$  Å,  $V = 350.0(1)$  Å<sup>3</sup> at 139 K and  $a = 8.3622(7)$ ,  $c = 5.0612(5)$  Å,  $V = 353.9(1)$  Å<sup>3</sup> at 286 K. 349 and 635 unique reflections refined to  $R(F) = 0.023$  and 0.019 at 139 and 286 K, respectively. The structure consists of infinite chains along  $c$ , built from corner sharing SeO<sub>3</sub>E tetrahedra, with E representing the Se lone pair. Observed bonding distances are Se–O(1) (\*2) 1.7926(4) [1.795(1)] and Se–O(2) 1.6226(9) [1.624(2)] Å at 286 [139] K. The shortest inter-chain distances, Se---O(2) 2.758(1) [2.743(2)] and (\*2) 2.857(1) [2.843(1)] Å at 286 [139] K, indicate considerable electrostatic interactions between chains. Including these next nearest oxygens the Se–O coordination can be described as distorted octahedral in a novel type of net. The final difference electron density map showed residual density in the predicted Se lone pair region.

### Introduction

The crystal structure of SeO<sub>2</sub> was determined by McCullough (1937) as being tetragonal,  $P4_2/mbc$ . The general properties of the structure at 120

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and 295 K were confirmed by Galy, Legros, Bertaud and Fischer (1978) and communicated by Legros and Galy (1978). The latter investigation suggested the non-centrosymmetric sub-group  $P4_2bc$  at room temperature.

The present investigation was undertaken in order to establish precise structural parameters for  $\text{SeO}_2$  at 139 and 286 K, and possibly to study experimentally the stereochemically important Se lone pair. Precise structural parameters and experimentally observed lone pair density will also provide a firm ground for theoretical studies of the electronic structure of solid  $\text{SeO}_2$ .

### Experimental

Single crystals of  $\text{SeO}_2$  were grown through sublimation in sealed glass tubes at 490 K giving prismatic (001) crystals bound by  $\{100\}$  and  $\{010\}$ . Due to water sensitivity (formation of  $\text{H}_2\text{SeO}_3$ ) the crystals were handled and mounted in dry Ar atmosphere. Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite monochromatized  $\text{MoK}\alpha$  radiation. The low temperature was attained with a locally built  $\text{N}_2$  gas blowing device also used at room temperature in order to provide a protective atmosphere for the crystal. The low temperature was calibrated at the  $\text{KH}_2\text{PO}_4$  phase transition. Unit cell dimensions between 130 and 290 K were determined from least-squares refinements of 50  $2\theta$  values with  $20^\circ \leq 2\theta \leq 60^\circ$  (Fig. 1). The 286 K data set was collected in a full sphere for  $2^\circ \leq 2\theta \leq 40^\circ$  ( $-8 \leq h, k \leq 8, -4 \leq l \leq 4$ ), one hemisphere for  $40^\circ \leq 2\theta \leq 70^\circ$  ( $-13 \leq h, k \leq 13, 0 \leq l \leq 8$ ), and the 500 estimated strongest reflections in one octant for  $70^\circ \leq 2\theta \leq 150^\circ$  ( $0 \leq h, k \leq 22, -13 \leq l \leq 0$ ).

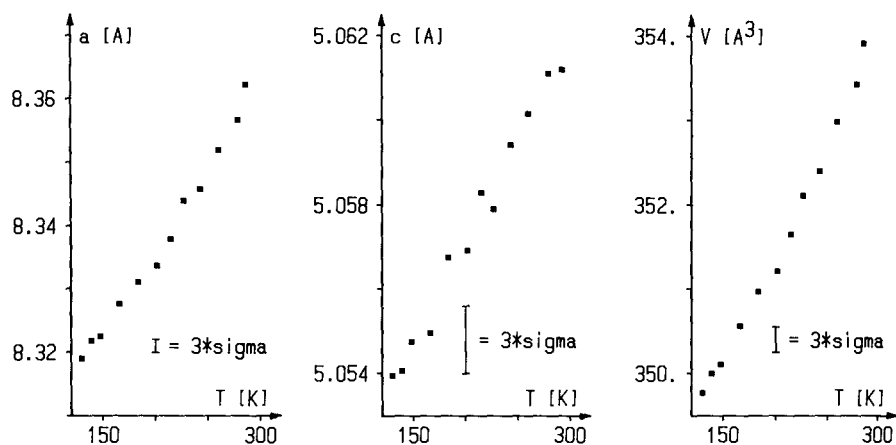


Fig. 1. Unit cell dimensions vs. temperature for  $\text{SeO}_2$ .

**Table 1.** Crystal data, data collection and least-squares refinement details for SeO<sub>2</sub>, space group  $P4_2/mbc$ ,  $Z = 8$ ,  $M_w = 110.96$ .

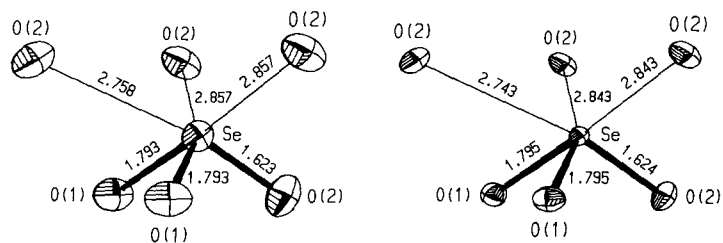
Temperature [K]	139(1)	286(1)
$a$ [Å]	8.3218(9)	8.3622(7)
$c$ [Å]	5.0541(6)	5.0612(5)
$V$ [Å <sup>3</sup> ]	350.0(1)	353.91(9)
$D_x$ [g cm <sup>-3</sup> ]	4.211	4.165
$\mu$ [MoK $\alpha$ ] [cm <sup>-1</sup> ]	207.6	205.3
Crystal size [mm <sup>3</sup> ]	0.06 · 0.06 · 0.05	0.10 · 0.08 · 0.26
Range of transmission factors	0.31–0.41	0.12–0.30
Scan widths [°]	0.8 + 0.35 tan $\theta$	0.6 + 0.35 tan $\theta$
Max sin $\theta/\lambda$ [Å <sup>-1</sup> ]	0.81	1.34
Isotropic extinction parameter	0.8(2) · 10 <sup>3</sup>	0.40(2) · 10 <sup>4</sup>
No of symmetry allowed reflections collected	2275	4057
with $I > \sigma(I)$ , “observed”	1738	3415
unique in final L.S. cycle	349	634
No of parameters refined	19	19
$R(F_{av})$	0.023	0.019
$R(F)$	0.036	0.025
$R(F^2)$	0.058	0.044
$R_w(F^2)$	0.094	0.061
$S$ [ $\Sigma w(\Delta F^2)^2/(n-m)$ ] <sup>1/2</sup>	1.01	1.05
Weighting constant, $c$	0.075	0.046

The 139 K data set was collected in one hemisphere for  $2^\circ \leq 2\theta \leq 70^\circ$  ( $-13 \leq h, k \leq 13, 0 \leq l \leq 8$ ). Reflections were measured using  $\omega/2\theta$  scans with constant  $4 \cdot 4$  mm<sup>2</sup> detector window, 4 min max time and requiring  $I > \sigma(I)$  in prescans in order to be considered “observed”. Two standard reflections measured every 6000 s of X-ray exposure time showed no systematic variations during either data collection. Both data sets were corrected for polarization and the Lorentz effect and for absorption using Gaussian integration. Internal agreement factors ( $R_{int} = \Sigma |I_{obs} - I_{aver}| / \Sigma I_{obs}$ ) when averaging symmetry equivalent reflections were 0.055 and 0.031 for the 139 and 286 K data sets, respectively.

Further information concerning crystal data, data collection and reduction and least-squares refinements are given in Table 1.

### Structure refinements

The full matrix least-squares refinements minimized  $\Sigma w(F_o^2 - F_c^2)^2$ , where  $w = [\sigma^2(F_o^2) + (cF_o^2)^2]^{-1}$  with  $\sigma(F_o^2)$  from counting statistics and  $c$  adjusted



**Fig. 2.** ORTEP (Johnson, 1976) drawings of the Se coordination in  $\text{SeO}_2$  at 286 (left) and 139 (right) K. The thermal ellipsoids are all scaled to include 75% probability.

**Table 2.** Final atomic coordinates ( $\cdot 10^5$ ) and anisotropic temperature factor coefficients ( $\cdot 10^5$ ) with estimated standard deviations for  $\text{SeO}_2$ .  $B_{\text{iso}} = 4 \sum_i \sum_j \beta_{ij} \cdot (a_j \cdot a_j) / 3$ . The temperature factor is of the form:

$$\exp - (\beta_{11} \cdot h_i^2 + \dots + 2 \cdot \beta_{ij} \cdot h_i \cdot h_j + \dots).$$

a) 286 K	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}} [\text{\AA}^2]$	Wyckoff position	
Se	13374(1)	21019(1)	0	0.950(2)	8 <i>h</i>	
O(1)	13802(6)	36198	25000	1.35(1)	8 <i>g</i>	
O(2)	-5710(11)	17507(12)	0	1.63(2)	8 <i>h</i>	
	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Se	338(1)	400(1)	770(4)	13(1)	0	0
O(1)	575(6)	575	808(25)	168(9)	130(10)	130
O(2)	381(9)	725(11)	1744(34)	-96(9)	0	0
b) 139 K	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}} [\text{\AA}^2]$	Wyckoff position	
Se	13396(3)	20929(3)	0	0.45(1)	8 <i>h</i>	
O(1)	13752(17)	36248	25000	0.74(3)	8 <i>g</i>	
O(2)	-5789(26)	17358(27)	0	0.90(4)	8 <i>h</i>	
	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Se	122(3)	154(3)	566(11)	5(2)	0	0
O(1)	262(15)	262	745(68)	55(21)	102(24)	102
O(2)	170(22)	366(25)	1178(80)	-39(20)	0	0

to give constant  $\langle w\Delta F^2 \rangle$  in different  $F_o^2$  and  $\sin\theta$  intervals. Following the recommendations by Schwarzenbach et al. (1989) the unaveraged data sets were used in the refinements.  $R(F_{\text{av}})$  in the following refers to the conventional  $R(F)$  using an averaged data set. The refinements were started

**Table 3.** Distances (Å) and angles (°) in SeO<sub>2</sub>.

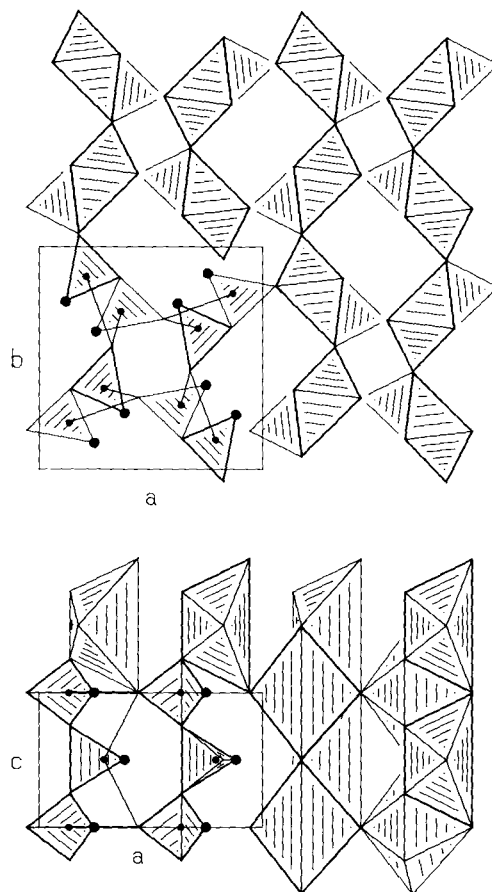
	139 K	286 K	McCullough (1937)
Bond distances and angles			
Se—O(1)	1.7951(10)	1.7926(4)	1.78(3)
Se—O(2)	1.6239(22)	1.6226(9)	1.73(8)
O(1)—Se—O(1)	89.48(5)	89.80(2)	90(0.5)
O(1)—Se—O(2)	98.41(7)	98.50(3)	98(2)
Se—O(1)—Se	121.26(8)	121.77(3)	125(0.5)
Shortest inter-chain distances			
Se—O(2) <sup>a</sup>	2.743(2)	2.758(1)	
Se—O(2) <sup>b,c</sup>	2.843(1)	2.857(1)	
O(1)—O(1) <sup>d</sup>	3.237(3)	3.264(1)	
O(1)—O(2) <sup>e,f</sup>	2.848(2)	2.863(1)	
O(2)—O(2) <sup>g</sup>	3.046(4)	3.080(2)	
O(2)—O(2) <sup>h,i,j,k</sup>	3.320(2)	3.338(1)	

<sup>a</sup>  $1/2+x, 1/2-y, z$ ; <sup>b</sup>  $y, -x, z+1/2$ ; <sup>c</sup>  $y, -x, z-1/2$ ; <sup>d</sup>  $-x, -y, z$ ; <sup>e</sup>  $y, -x, z+1/2$ ;  
<sup>f</sup>  $1/2+x, 1/2-y, z$ ; <sup>g</sup>  $1-x, -y, z$ ; <sup>h</sup>  $1-y, x, z+1/2$ ; <sup>i</sup>  $1-y, x, z-1/2$ ; <sup>j</sup>  $1+y, -x, z+1/2$ ;  
<sup>k</sup>  $1+y, -x, z-1/2$ .

with parameters from Galy, Legros, Bertaud and Fischer (1978). The 19 parameters used in the final least-squares cycles included positional and anisotropic thermal parameters, one scale factor and one isotropic extinction parameter (type I, Lorentzian mosaicity, Becker and Coppens, 1974). The largest (parameter shift)/(parameter e.s.d.) in the final cycle was <0.03 and the highest absolute peaks in the final difference electron density maps were 1.48 and 1.09 eÅ<sup>-3</sup> for the 139 and 286 K data sets respectively. Refinements in the non-centric space groups *P4<sub>2</sub>bc*, *P4<sub>2</sub>1c*, *P4<sub>2</sub>2<sub>1</sub>2* and *P4b2* did not improve the results from any of the data sets. Introducing one additional spherical term per atom in a Hirshfeld type refinement [Hirshfeld, 1977, exponential radial dependence with fixed exponential factors of 2.5 (Se) and 5.5 (O)] reduced  $R_w(F^2)$  from 0.0607 to 0.0592 for the 286 K data set.

Scattering factors for neutral atoms and anomalous scattering corrections were taken from International Tables for X-ray Crystallography. The crystallographic computer programs have been described by Lundgren (1983). Final atomic parameters are given in Table 2.<sup>1</sup>

<sup>1</sup> Lists of observed and calculated structure factors can be ordered referring to CSD 55716, citing authors and journal at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.



**Fig. 3.** Projections of the crystal structure of  $\text{SeO}_2$ . Drawn using tetrahedra inside the outlined unit cell and using octahedra outside. Small filled circles = Se and large filled circles = lone pair position following Galy et al. (1975). The shortest inter-chain  $\text{Se}-\text{O}(2)$  distances are indicated as straight lines.

### Discussion

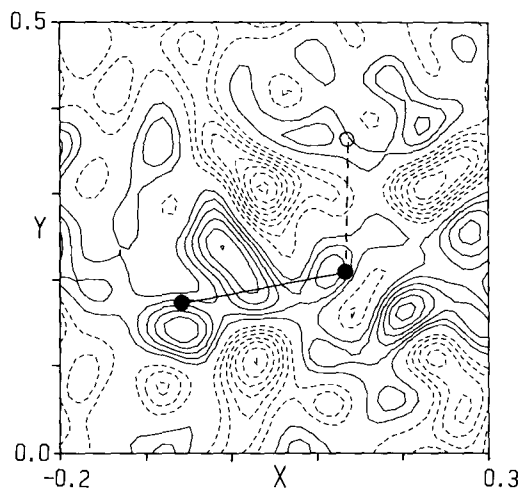
The Se atom is bonded to three O atoms forming an  $\text{SeO}_3$  pyramid. The Se environment can also be described as irregularly tetrahedral, with three oxygens and one lone pair (E) at the vertices. The  $\text{SeO}_3\text{E}$  tetrahedra are linked through corner sharing into infinite isolated chains along  $c$ ,  $\dots -\text{O}(1)-\text{Se}[\text{O}(2)\text{E}]-\text{O}(1)-\text{Se}[\text{O}(2)\text{E}]-\text{O}(1)-\dots$  (c.f.  $\text{CrO}_3$ , Stephens and Cruickshank, 1970). Two projections of the tetrahedral packing are

shown within the unit cells outlined in Figure 3. The shortest interchain Se–O(2) distances, 2.758(1) and (\*2) 2.857(1) Å, are considerably shorter than the sum of the Se and O van der Waals radii, 3.4 Å. Hirshfeld refinements restricted to spherical terms gave net charges of +0.51(4) on Se, –0.21(3) on O(1) and –0.32(4) on O(2) suggesting considerable electrostatic interactions between chains. Adding the three next nearest oxygens to the covalently bonded ones the Se–O coordination can be described as distorted octahedral (Fig. 2). The resulting octahedral net is shown in Figure 3.

The observed covalent Se–O distances can be compared to those found in hydrogen selenite compounds, e.g. 1.643(2), 1.735(2), 1.743(2) Å in H<sub>2</sub>SeO<sub>3</sub> (neutron data, Larsen, Lehmann and Sötofte, 1971); 1.665(3), 1.786(4), 1.670(3) Å in Zn(HSeO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (neutron data, Kondrashev, Nozik, Fykin and Shibanova, 1979); 1.678(4), 1.673(5), 1.773(5) Å in Cu(HSeO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (X-ray data, Hiltunen, Leskelä, Niinistö and Tammenmaa, 1985). The Se–O(2) distance in SeO<sub>2</sub> is slightly shorter than the short Se–O distances in the hydrogen selenites due to hydrogen bonding and/or metal coordination in the latter. On the other hand the Se–O(2) distance is slightly longer than that of free SeO<sub>2</sub>, 1.607(1) Å (Takeo, Hirota and Morino, 1970). The Se–O(1) distance is slightly longer than the longer Se–O distances in the hydrogen selenites since O(1) is bonded to two Se instead of one Se and one H in the hydrogen selenites. The average Se–O bonding distance in the hydrogen selenites is 1.707 Å as compared to 1.736 Å in SeO<sub>2</sub>. This difference is similar to that observed in a comparison of S–O distances in sulphates and in S<sub>3</sub>O<sub>9</sub>, 1.48–1.49 Å and 1.513 Å, respectively (McDonald and Cruickshank, 1967), and can be attributed to the increase in bond length to the shared oxygen in the condensed compounds.

While the Se–O bonding distances appear independent of temperature, the O(1)–Se–O(1) and Se–O(1)–Se angles are slightly, but significantly increased when going from 139 to 286 K. The average ratios between temperature factor coefficients at 286 and 139 K are as expected larger perpendicular to the chain direction (*a* and *b* directions), 2.3, than parallel to the chain (*c* direction), 1.3. The larger temperature factor coefficients in the *a* and *b* directions at 286 K are also reflected in increased interchain distances and consequently in a larger increase in the *a* (*b*) axis as compared to the *c* axis when increasing the temperature (c.f. Fig. 1).

A difference electron density map in the plane *z* = 0 (Fig. 4) revealed residual density in the predicted Se lone pair region as well as residual densities in the Se–O(2) bonding and the O(2) lone pair region. The steric influence of the Se lone pair is well established, c.f. summary by Galy, Meunier, Andersson and Åström (1975). An electronic description of the Se lone pair and the bonding in solid SeO<sub>2</sub> is however not straightforward. The 4*s* and 4*p* densities, as obtained from Extended Hückel calculations, are far too diffuse to cause a detectable difference electron density in an X-ray



**Fig. 4.** Difference electron density map of  $\text{SeO}_2$  at 286 K in the plane  $z = 0$ . Levels at  $0.1 \text{ e}/\text{\AA}^3$ . Zero levels omitted, negative levels broken. Filled circles: O(2) (left) and Se (right); open circle: O(1), 1.26 Å above and below the plane.

diffraction experiment. An ab initio calculation of the electronic structure of solid  $\text{SeO}_2$  will therefore be attempted.

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