

343. The Crystal Structures of ThSe₂ and Th₇Se₁₂.

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The crystal structures of ThSe₂ and Th₇Se₁₂ have been determined from powder photographs obtained by use of Guinier-type focusing cameras. ThSe₂ is orthorhombic with $a = 4.411 \pm 0.002$ kX, $b = 7.595 \pm 0.002$ kX, $c = 9.046 \pm 0.002$ kX. There are 4 molecules per unit cell and the space-group is $D_{2h}^{16}-Pmnb$. Th₇Se₁₂ is hexagonal with $a = 11.546 \pm 0.006$ kX $c = 4.22 \pm 0.01$ kX. There is one molecule per unit cell and the space-group is $C_{6h}^2-P6_3/m$. Both compounds are thus isostructural with their corresponding sulphides.

In a recent report (D'Eye, Sellman, and Murray, *J.*, 1952, 2555) of an investigation of the Th-Se system the compounds ThSe₂ and Th₇Se₁₂ were described. However, owing to the poor powder-diffraction data obtained from Debye-Scherrer photographs it was then not possible to determine unambiguously the crystal structures of these two compounds. Through the courtesy of Professor G. Hägg in allowing me to work at his Institute in Uppsala University, Sweden, it has been possible to obtain good diffraction data by use of Guinier-type focusing cameras which necessarily eliminate the spacing errors caused by absorption in the specimen. It was tentatively suggested in the previous communication that Th₇Se₁₂ and ThSe₂ had hexagonal and orthorhombic lattices, respectively, and that they were isostructural with their corresponding sulphides. This has now been established.

EXPERIMENTAL

X-Ray photographs were obtained by using Guinier-type focusing cameras with a bent quartz-crystal monochromator and Cu-K α radiation. The intensities of the resulting diffraction lines were visually estimated. The expression for the intensity of a diffraction line on a Guinier-type photograph is $I_c \propto A_1 A_2 \rho F^2 (1 + \cos^2 2\theta_m \cos^2 2\theta) / \sin^2 \theta \cos \theta$, where I_c , θ , θ_m , A_1 , A_2 , ρ , and F are respectively the calculated intensity, Bragg angle, the angle the X-ray beam from the anti-cathode makes with the monochromator (for Cu, $\theta_m = 13^\circ 21'$), absorption factor for specimen, absorption factor for film emulsion, multiplicity constant, and structure factor (Hägg, personal communication); but for cases where the absorption in the specimen is low (in this case because of the extreme thinness of the specimen) and where extreme accuracy is not required the expression simplifies to $I_c \propto \rho F^2 (1 + \cos^2 2\theta_m \cos^2 2\theta) / \sin^2 \theta \cos \theta$, and this expression has been used throughout in calculating intensities.

The diffraction patterns of both compounds were indexed by using the mathematical methods of Hesse (*Acta Cryst.*, 1948, 1, 200) and of Henry, Lipson, and Wooster ("Interpretation of X-Ray Diffraction Photographs," Macmillan, 1951).

DISCUSSION

(1) *Structure of ThSe₂*.—The diffraction pattern was indexed on the basis of an orthorhombic lattice with $a = 4.411 \pm 0.002$, $b = 7.595 \pm 0.002$, $c = 9.046 \pm 0.002$ kX. From Table 1 it is seen that the agreement between observed and calculated $\sin^2 \theta$ values is good. The number of molecules per unit cell is 4, giving a calculated density of 8.5 g./c.c. (observed, 8.2 g./c.c.). The absences in the observed indices of the reflections indicate that the space-group is $D_{2h}^{16}-Pmnb$. The thorium and selenium atoms will be on the 4(c) special position ("International Tables for X-Ray Crystallography, Vol. 1). Intensities calculated with the parameters having the values:

	x	y		x	y		x	y
Th	0.25	0.125	Se ₁	0.38	0.43	Se ₁₁	0.47	0.82

are seen from Table 1 to be in good agreement with the observed intensities. ThSe₂ is therefore isostructural with ThS₂ (Zachariasen, *Acta Cryst.*, 1949, 2, 291).

The thorium atom is thus surrounded by nine selenium atoms at a mean distance of 3.08 kX [cf. the Th-Se distances in ThOSe and ThSe which are respectively 3.15 and 2.93 kX (D'Eye *et al.*, *loc. cit.*). The individual Th-Se distances (kX) are:

Th-2 Se ₁ = 2.98	Th-Se ₁ = 2.85	Th-2 Se ₁₁ = 3.09
Th-Se ₁ = 2.93	Th-Se ₁₁ = 3.22	Th-2 Se ₁₁ = 3.27

(2) *Structure of Th₇Se₁₂.*—The powder diffraction pattern was indexed on the basis of a hexagonal cell with $a = 11.546 \pm 0.006$ and $c = 4.22 \pm 0.01$ kX. The agreement between observed and calculated $\sin^2\theta$ values is seen from Table 2 to be good. If the formula is Th₇Se₁₂ there will be one molecule per unit cell, giving a calculated density of 8.7 g./c.c. The compounds ThSe, ThSe₂, and ThOSe are all isostructural with their corresponding sulphides. It would therefore seem a reasonable assumption that Th₇Se₁₂ is isostructural with Th₇S₁₂ (Zachariasen, *loc. cit.*, p. 288). The structure of Th₇S₁₂ was

TABLE 1. (ThSe₂).

<i>hkl</i>	$\sin^2\theta$, obs.	$\sin^2\theta$, calc.	<i>I</i> , obs.	<i>I</i> , calc.	<i>hkl</i>	$\sin^2\theta$, obs.	$\sin^2\theta$, calc.	<i>I</i> , obs.	<i>I</i> , calc.
011	—	0175	—	2	131	1301	1299	w+	38
002	—	0289	—	0	123	1365	1365	w+	18
101	0377	0376	m	35	202	—	1505	—	0
012	0392	0392	s	71	024	—	1567	—	16
020	0410	0410	m	24	114	1567	{ 1564 }	w	{ 0
111	0479	{ 0479 }	s-	{ 51	033	—	1574	—	1
021	—	{ 0482 }	—	{ 0	212	1612	1608	w	24
112	—	{ 0696 }	—	{ 27	040	1637	1640	diffuse	vw
022	0694	{ 0699 }	m	{ 2	133	1877	1879	„	vwv
120	0714	0714	w	14	140	1950	1944	„	vwv
013	0749	0753	vw	8	141	2019	2016	„	vwv
121	0787	0786	s+	100	115	—	2214	—	—
103	0955	0955	m	52	025	2213	{ 2217 }	„	vw
031	0995	0995	w-	4	231	—	2211	—	—
122	—	1003	—	2	204	2375	2373	„	w
113	—	{ 1058 }	—	{ 46	232	2434	2428	„	m
023	1056	{ 1061 }	m	{ 5	125	2519	2521	„	vw
004	1156	1157	w	16	016	2701	2705	„	vw
032	1209	1212	s	54	233	2790	2790	„	w
200	1217	1216	m	41	052	—	2852	—	—
014	—	1259	—	1	240	2858	{ 2856 }	„	w

determined from single-crystal data (*idem, ibid.*) and has the space-group $C_{6h}^2-P6_3/m$ with 1 Th on the position 2(*a*) and 6 Th as well as 6 S₁ and 6 S₁₁ on three positions 6(*h*). The structure exhibits disorder with the one thorium atom on either $00\frac{1}{2}$ or $00\frac{3}{4}$.

It was noted that in the case of Th₇Se₁₂ the absences in the observed indices of the reflections were compatible with the space group $C_{6h}^2-P6_3/m$ and the thorium and selenium atoms were accordingly placed on positions 2(*a*) and 6(*c*) and with practically the same parameters as were found for Th₇S₁₂. The parameters used have the values given below :

	<i>x</i>	<i>y</i>		<i>x</i>	<i>y</i>		<i>x</i>	<i>y</i>
6 Th ₁₁	0.15	-0.28	6 Se ₁	0.51	0.38	6 Se ₁₁	0.24	0.0

Intensities calculated by using these values give fair agreement with the observed intensities, it being borne in mind that the parameters have not been refined for the present case (see Table 2).

TABLE 2. (Th₇Se₁₂).

<i>hkl</i>	$\sin^2\theta$, obs.	$\sin^2\theta$, calc.	<i>I</i> , obs.	<i>I</i> , calc.	<i>hkl</i>	$\sin^2\theta$, obs.	$\sin^2\theta$, calc.	<i>I</i> , obs.	<i>I</i> , calc.
010	—	0059	—	0	311	1103	1104	s-	38
110	—	0178	—	0	320	1124	1125	vwv	1
020	—	0237	—	0	410	1242	1243	s	78
101	0392	0393	w	23	041	1279	1281	vw	11
210	0412	0414	s	100	002	1338	1336	vw+	34
111	0512	0512	vw	16	102	—	1395	—	0
030	0530	0533	vw	1	321	1460	1459	diffuse	w
021	0570	0571	w	41	420	1656	1658	„	m
220	0709	0710	vw	3	501	1814	1814	„	vw
211	0746	0748	s	80	421	1995	1992	„	w
310	0766	0770	vw	4	511	2172	2169	„	w
031	0865	0867	s	57	520	2310	2309	„	w
040	0948	0947	w-	5	431	2525	2524	„	m
221	1044	1044	s-	33	521	2646	2643	„	m

$\text{Th}_7\text{Se}_{12}$ is therefore isostructural with Th_7S_{12} , with Th_1 surrounded by 9 Se_{11} atoms and Th_{11} by 3 Se_{11} and 5 Se_1 atoms. The individual distances can be calculated (in kX) as :

$$\begin{array}{llll} \text{Th}_{11}-\text{Se}_1 = 3.00 & \text{Th}_{11}-\text{Se}_{11} = 2.89 & \text{Th}_1-3 \text{Se}_{11} = 2.77 & \text{Mean Th}_{11}-\text{Se} = 3.07 \text{ kX} \\ \text{Th}_{11}-4 \text{Se}_1 = 3.20 & \text{Th}_{11}-2\text{Se}_{11} = 2.92 & \text{Th}_1-6 \text{Se}_{11} = 3.48 & \end{array}$$

The Th_{11} -Se distances are compatible with the Th-Se distances observed in the compounds ThOSe , ThSe , and ThSe_2 but the Th_1 - Se_{11} distances are either too low or too high. It appears that, as in the case of Th_7S_{12} (Zachariassen, *loc. cit.*), the Se_{11} atoms must be displaced from their mean positions, the direction depending on whether the $00\frac{1}{4}$ or the $00\frac{3}{4}$ position is occupied by the thorium atom. The suggested new Se_{11} positions are given below for the case where the $00\frac{1}{4}$ position is occupied by Th.

$$\begin{array}{l} 6 \text{Se}_{11} \text{ on } 0.27, 0, 0.25; 0, 0.27, 0.25; 0.73, 0.73, 0.25 \\ \quad \quad \quad \overline{0.21}, 0, 0.75; 0, \overline{0.21}, 0.75; 0.21, 0.21, 0.75 \end{array}$$

The interatomic distances for Th_1 - Se_{11} will now be: $\text{Th}_1-3 \text{Se}_{11} = 3.12 \text{ kX}$, $\text{Th}_1-6 \text{Se}_{11} = 3.20 \text{ kX}$; mean Th_1 - $\text{Se}_{11} = 3.17 \text{ kX}$, which are compatible with other Th-Se distances.

Conclusion.—The results now given add considerable weight to the view expressed earlier (D'Eye *et al.*, *loc. cit.*) that the Th-Se system is closely analogous to the Th-S system (Eastman *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 4019).

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