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The Crystal Structure of Triuranium Pentaselenide

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Triuranium pentaselenide, U_3Se_5 , crystallizes with an orthorhombic unit cell; $a_o = 12.43$ (2), $b_o = 8.48$ (1) and $c_o = 7.77$ (1) Å, $Z = 4$, space group probably *Pnma*. Two environmentally distinct types of uranium atom and two environmentally distinct types of selenium atom are found in the structure. Uranium-selenium interatomic distances range from 2.80 to 3.18 Å, varying with the coordination numbers of the atoms involved. The final R value for 615 reflexions, observed by the equi-inclination Weissenberg method, is 0.114.

Introduction

During recent years considerable attention has been devoted to the chalcogenides of uranium, largely as a

result of the complex structural and bonding problems posed by these apparently simple binary compounds. The crystal chemistry of actinide chalcogenides has been surveyed (Dell & Bridger, 1971) and these com-

pounds may be classified for the most part in terms of known structure types. A notable exception, however, is provided by the selenide U_3Se_5 which, on the basis of X-ray powder data, is believed to be isomorphous with U_3S_5 (Khodadad, 1961) and Np_3S_5 (Marcon, 1967). Since this structure type had not hitherto been fully described, it appeared to merit a single-crystal structural investigation.

Experimental

U_3Se_5 single crystals, prepared* by a vapour-phase iodine transport method at 900°C in a sealed silica apparatus, were ground approximately spherical in a compressed-air driven race with an abrasive wall. The black crystal used for data collection was 0.2 mm in diameter and as near spherical as could be judged by microscopic observation.

The unit-cell parameters and systematic absences, obtained from Weissenberg and precession photographs using $Cu K\alpha$ radiation ($\lambda=1.5405 \text{ \AA}$) were:

$$\begin{aligned} a_o &= 12.43 \pm 0.02, \quad b_o = 8.48 \pm 0.01, \quad c_o = 7.77 \pm 0.01 \text{ \AA} \\ 0kl &\text{ reflexions absent for } k+l \text{ odd} \\ hk0 &\text{ reflexions absent for } h \text{ odd.} \end{aligned}$$

This suggested that the space group was either $Pnma$ or $Pna2_1$. $Pnma$ was selected on the basis of the structure refinement described below.

ρ (calculated) was 8.99 g.cm^{-3} for $Z=4$ which compares favourably with the value for ρ (observed) of 9.04 g.cm^{-3} recorded elsewhere (Mazurier & Khodadad, 1968).

Taking the mass absorption coefficient for uranium as $128 \text{ cm}^2.\text{g}^{-1}$ (Roof, 1959), the linear absorption coefficient for $Mo K\alpha$ radiation is 980.4 cm^{-1} .

Partial three-dimensional intensity data were re-

corded by the equi-inclination Weissenberg method using zirconium-filtered molybdenum radiation for reciprocal lattice nets nkl for $n=0$ to 9 inclusive. Intensities from different layers were brought on to an approximately common scale by factors inversely proportional to the exposure times. An empirical correction was made for $\alpha_1-\alpha_2$ splitting whereby measured intensities attributable to α_1 only were multiplied by the factor 1.34. 615 intensities were estimated visually by comparison with a calibrated scale and corrected for Lorentz and polarization effects. To compensate for anisotropic absorption effects, the specimen crystal was treated as a sphere and the structure amplitudes were corrected by interpolation from the curves given in *International Tables for X-ray Crystallography* (Bond, 1959).

Solution and refinement of the structure

Positional parameters were assigned to the uranium atoms after consideration of the three-dimensional Patterson function. At this stage it was not possible to decide between the two space groups, and three uranium atoms were placed in general positions of the non-centrosymmetric alternative $Pna2_1$. An electron-density map revealed the five selenium atoms maintaining a configuration very close to that required by the extra symmetry of $Pnma$. The structure was therefore initially refined in each space group and the results compared.

The scattering factors for uranium and selenium (Hanson, Herman, Lea & Skillman, 1964) were modified by the real parts of the anomalous dispersion corrections (Cromer, 1964), but the full-matrix, least-squares program (Bracher & Taylor, 1967) employed was not equipped to deal with the imaginary part, which was therefore not introduced at this stage. All reflexions were weighted equally and all atoms refined with isotropic temperature factors. After each cycle of refinement, individual layer scale factors were recal-

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Table 1. Refinement in the alternative space groups

Positional parameters ($\times 10^4$) and thermal parameters ($\times 10^3$). $B=8\pi^2u$.

$Pna2_1$

Atom	Wyckoff notation	x/a	y/b	z/c	$B(\text{\AA}^2)$
U(1)	4(a)	1781 (8)	277 (8)	0 (0)	108 (57)
U(2)	4(a)	102 (5)	5758 (5)	2585 (12)	672 (66)
U(3)	4(a)	3230 (14)	5299 (15)	-43 (14)	2123 (120)
Se(1)	4(a)	4036 (21)	1675 (21)	510 (22)	333 (225)
Se(2)	4(a)	1878 (15)	3315 (16)	2530 (48)	1423 (195)
Se(3)	4(a)	5010 (13)	5402 (12)	2434 (27)	900 (205)
Se(4)	4(a)	2816 (14)	8092 (14)	2600 (40)	1010 (199)
Se(5)	4(a)	4138 (30)	1718 (34)	4658 (33)	1959 (484)

$Pnma$ (b and c axes interchanged)

U(1)	8(d)	1777 (3)	-1 (5)	283 (3)	879 (37)
U(2)	4(c)	101 (5)	2500 (0)	5756 (5)	643 (54)
Se(1)	8(d)	4075 (9)	440 (9)	1694 (9)	931 (107)
Se(2)	4(c)	1874 (15)	2500 (0)	3327 (16)	1391 (183)
Se(3)	4(c)	5014 (13)	2500 (0)	5407 (12)	937 (157)
Se(4)	4(c)	2823 (13)	2500 (0)	8082 (14)	919 (162)

culated to make $|kF_o| = |F_c|$ for each layer. Values for k ranged from 0.38 to 0.50.

The refinements converged with R at 0.113 for $Pna2_1$ and at 0.122 for $Pnma$ (fewer atomic parameters to refine). The positional parameters, given in Table 1, were similar in the two cases, but the isotropic thermal parameters, also given in Table 1, showed consider-

Table 2. Atomic parameters for U_3Se_5 ($Pnma$) with standard deviations in parentheses

(a) Positional parameters ($\times 10^4$)

	x/a	y/b	z/c
U(1)	1775 (2)	-1 (3)	285 (3)
U(2)	97 (3)	2500 (0)	5755 (3)
Se(1)	4064 (6)	444 (6)	1691 (6)
Se(2)	1874 (10)	2500 (0)	3328 (12)
Se(3)	5003 (10)	2500 (0)	5387 (9)
Se(4)	2842 (9)	2500 (0)	8074 (10)

(b) Vibrational parameters ($\times 10^4$)

$$B_{ij} = 2\pi^2(a^*)^2 U_{11} \text{ etc.}$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U(1)	13 (3)	35 (2)	31 (2)	2 (3)	8 (3)	0 (5)
U(2)	16 (4)	30 (2)	14 (2)	0 (0)	0 (4)	0 (0)
Se(1)	-2 (7)	35 (5)	36 (6)	-16 (7)	9 (7)	-8 (8)
Se(2)	28 (12)	42 (10)	53 (11)	0 (0)	-2 (14)	0 (0)
Se(3)	37 (13)	29 (8)	32 (8)	0 (0)	9 (13)	0 (0)
Se(4)	15 (11)	34 (9)	32 (8)	0 (0)	13 (11)	0 (0)

able differences, with the values from the $Pnma$ refinement falling more clearly into two sets according to atom type. After consideration of all the preceding factors the space group $Pnma$ was adopted for further refinement of the structure.

Substitution of the U^{4+} and Se^{2-} ionic scattering curves for the neutral atom curves scarcely influenced the atomic parameters. The ionic scattering curves were retained however, since they appeared to be more appropriate to the emerging structure.

The imaginary component of the anomalous-dispersion correction (Cromer, 1964) was included in the further refinement by means of a program using the block-diagonal approximation (Ahmed, Hall, Pippy & Saunderson, 1968). An analysis of the discrepancy between $|F_o|$ and $|F_c|$ indicated that the differences were not concentrated in any particular region of $\sin \theta/\lambda$ and a straightforward weighting scheme was adopted: $/w=1$ if $|F_o| \leq 60$, $/w=60/|F_o|$ if $|F_o| > 60$.

Finally, the process of readjusting the layer scales between cycles was discontinued and all atoms were refined with anisotropic temperature factors. After 3 cycles, all the parameter shifts were less than $\frac{1}{3}$ of their corresponding standard deviations. The final value of R was 0.114. The atomic parameters, together with their standard deviations, are given in Table 2. The

Table 3. Observed and calculated structure amplitudes

The asterisk indicates unobserved reflexions for which $I_o = \frac{1}{2} I_m$.

H	K	L	I_{OFO}	I_{IFC}	H	K	L	I_{OFO}	I_{IFC}	H	K	L	I_{OFO}	I_{IFC}
2	2	2	220	172	2	2	2	175	145	2	2	2	107	175
2	2	2	109	72	2	2	2	145	115	2	2	2	109	175
2	2	2	115	108	2	2	2	145	115	2	2	2	109	175
2	2	2	122	174	2	2	2	145	115	2	2	2	109	175
2	2	2	125	91	2	2	2	145	115	2	2	2	109	175
2	2	2	126	21	2	2	2	145	115	2	2	2	109	175
2	2	2	127	104	2	2	2	145	115	2	2	2	109	175
2	2	2	128	37	2	2	2	145	115	2	2	2	109	175
2	2	2	129	91	2	2	2	145	115	2	2	2	109	175
2	2	2	130	27	2	2	2	145	115	2	2	2	109	175
2	2	2	131	25	2	2	2	145	115	2	2	2	109	175
2	2	2	132	27	2	2	2	145	115	2	2	2	109	175
2	2	2	133	25	2	2	2	145	115	2	2	2	109	175
2	2	2	134	27	2	2	2	145	115	2	2	2	109	175
2	2	2	135	25	2	2	2	145	115	2	2	2	109	175
2	2	2	136	27	2	2	2	145	115	2	2	2	109	175
2	2	2	137	25	2	2	2	145	115	2	2	2	109	175
2	2	2	138	27	2	2	2	145	115	2	2	2	109	175
2	2	2	139	25	2	2	2	145	115	2	2	2	109	175
2	2	2	140	27	2	2	2	145	115	2	2	2	109	175
2	2	2	141	25	2	2	2	145	115	2	2	2	109	175
2	2	2	142	27	2	2	2	145	115	2	2	2	109	175
2	2	2	143	25	2	2	2	145	115	2	2	2	109	175
2	2	2	144	27	2	2	2	145	115	2	2	2	109	175
2	2	2	145	25	2	2	2	145	115	2	2	2	109	175
2	2	2	146	27	2	2	2	145	115	2	2	2	109	175
2	2	2	147	25	2	2	2	145	115	2	2	2	109	175
2	2	2	148	27	2	2	2	145	115	2	2	2	109	175
2	2	2	149	25	2	2	2	145	115	2	2	2	109	175
2	2	2	150	27	2	2	2	145	115	2	2	2	109	175
2	2	2	151	25	2	2	2	145	115	2	2	2	109	175
2	2	2	152	27	2	2	2	145	115	2	2	2	109	175
2	2	2	153	25	2	2	2	145	115	2	2	2	109	175
2	2	2	154	27	2	2	2	145	115	2	2	2	109	175
2	2	2	155	25	2	2	2	145	115	2	2	2	109	175
2	2	2	156	27	2	2	2	145	115	2	2	2	109	175
2	2	2	157	25	2	2	2	145	115	2	2	2	109	175
2	2	2	158	27	2	2	2	145	115	2	2	2	109	175
2	2	2	159	25	2	2	2	145	115	2	2	2	109	175
2	2	2	160	27	2	2	2	145	115	2	2	2	109	175
2	2	2	161	25	2	2	2	145	115	2	2	2	109	175
2	2	2	162	27	2	2	2	145	115	2	2	2	109	175
2	2	2	163	25	2	2	2	145	115	2	2	2	109	175
2	2	2	164	27	2	2	2	145	115	2	2	2	109	175
2	2	2	165	25	2	2	2	145	115	2	2	2	109	175
2	2	2	166	27	2	2	2	145	115	2	2	2	109	175
2	2	2	167	25	2	2	2	145	115	2	2	2	109	175
2	2	2	168	27	2	2	2	145	115	2	2	2	109	175
2	2	2	169	25	2	2	2	145	115	2	2	2	109	175
2	2	2	170	27	2	2	2	145	115	2	2	2	109	175
2	2	2	171	25	2	2	2	145	115	2	2	2	109	175
2	2	2	172	27	2	2	2	145	115	2	2	2	109	175
2	2	2	173	25	2	2	2	145	115	2	2	2	109	175
2	2	2	174	27	2	2	2	145	115	2	2	2	109	175
2	2	2	175	25	2	2	2	145	115	2	2	2	109	175
2	2	2	176	27	2	2	2	145	115	2	2	2	109	175
2	2	2	177	25	2	2	2	145	115	2	2	2	109	175
2	2	2	178	27	2	2	2	145	115	2	2	2	109	175
2	2	2	179	25	2	2	2	145	115	2	2	2	109	175
2	2	2	180	27	2	2	2	145	115	2	2	2	109	175
2	2	2	181	25	2	2	2	145	115	2	2	2	109	175
2	2	2	182	27	2	2	2	145	115	2	2	2	109	175
2	2	2	183	25	2	2	2	145	115	2	2	2	109	175
2	2	2	184	27	2	2	2	145	115	2	2	2	109	175
2	2	2	185	25	2	2	2	145	115	2	2	2	109	175
2	2	2	186	27	2	2	2	145	115	2	2	2	109	175
2	2	2	187	25	2	2	2	145	115	2	2	2	109	175
2	2	2	188	27	2	2	2	145	115	2	2	2	109	175
2	2	2	189	25	2	2	2	145	115	2	2	2	109	175
2	2	2	190	27	2	2	2	145	115	2	2	2	109	175
2	2	2	191	25	2	2	2	145	115	2	2	2	109	175
2	2	2	192	27	2	2	2	145	115	2	2	2	109	175
2	2	2	193	25	2	2	2	145	115	2	2	2	109	175
2	2	2	194	27	2	2	2	145	115	2	2	2	109	175
2	2	2	195	25	2	2	2	145	115	2	2	2	109	175
2	2	2	196	27	2	2	2	145	115	2	2	2	109	175
2	2	2	197	25	2	2	2	145	115	2	2	2	109	175
2	2	2	198	27	2	2	2	145	115	2	2	2	109	175
2	2	2	199	25	2	2	2	145	115	2	2	2	109	175
2	2	2	200	27	2	2	2	145	115	2	2	2	109	175
2	2	2	201	25	2	2	2	145	115	2	2	2	109	175
2	2	2	202	27	2	2	2	145	115	2	2	2	109	175
2	2	2	203	25	2	2	2	145	115	2	2	2	109	175
2	2	2	204	27										

Table 3 (*cont.*)

single anomalously low temperature parameter [B_{11} for Se(1)] may be due to residual anisotropic absorption effects. The final values of the observed and calculated structure amplitudes are given in Table 3.

A difference synthesis computed towards the end of the refinement showed no peaks greater than two electrons.

Discussion

The final values of the short interatomic distances are given in Table 4 together with their estimated standard deviations. Angles at the selenium atoms are given in Table 5.

The essential features of the structure are shown in Fig. 1 which is a view down the [001] direction. U(1) is surrounded by eight near-neighbour selenium atoms at a mean distance of 3.08 ± 0.02 Å while U(2) has seven near neighbours at a mean distance of 2.89 ± 0.03 Å. There are no other U-Se distances shorter than 3.86 Å. Se(1) has four near-neighbour uranium atoms at a mean distance of 2.94 Å and Se(2), Se(3) and Se(4) each have five near-neighbour uranium atoms at a mean distance of 3.06 Å.

The shortest Se-Se distances (3.40–3.64 Å) are all comparable with the shortest non-bonding contacts (3.46 Å) in elemental selenium and much greater than the Se-Se bond length (2.32 Å) (Wyckoff, 1965). The shortest U-U contacts (4.24 Å) are much longer than the bonding distances (2.76 Å) in α -uranium (Sturcken & Post, 1960).

In a structure lacking major three-dimensional discontinuity it is far less likely that the arrangement of seven or eight near neighbours around a metal atom

Table 4. Interatomic distances (\AA) with standard deviations in parentheses

Due to the large number of equivalent positions involved, the fractional coordinates of each atom are given and a system of primes is avoided for both this table and Fig. 1.

(a) U–Se distances

Atom 1	x/a	y/b	z/c	Atom 2	x/a	y/b	z/c	Distance
U(1)	0.1775	-0.0001	0.0285	Se(1)	0.4064	0.0444	0.1691	3.07 (0-01)
U(1)	0.1775	-0.0001	0.0285	Se(2)	0.1874	0.2500	0.3328	3.18 (0-01)
U(1)	0.1775	-0.0001	0.0285	Se(4)	0.2842	0.2500	0.8074	3.04 (0-01)
U(1)	0.6775	0.5001	0.4715	Se(3)	0.5003	0.2500	0.5387	3.10 (0-01)
U(1)	0.3226	0.4999	0.5285	Se(2)	0.1874	0.2500	0.3328	3.10 (0-01)
U(1)	0.3226	0.4999	0.5285	Se(3)	0.5003	0.2500	0.5387	3.06 (0-01)
U(1)	0.3226	0.4999	0.5285	Se(4)	0.2842	0.2500	0.8074	3.07 (0-01)
U(1)	0.3226	0.0001	0.5285	Se(1)	0.4064	0.0444	0.1691	3.00 (0-01)
U(2)	0.0097	0.2500	0.5755	Se(2)	0.1874	0.2500	0.3328	2.91 (0-01)
U(2)	0.5097	0.2500	0.9245	Se(3)	0.5003	0.2500	0.5387	3.00 (0-01)
U(2)	0.5097	0.2500	0.9245	Se(4)	0.2842	0.2500	0.8074	2.95 (0-01)
U(2)	0.5097	0.2500	-0.0755	Se(1)	0.4064	0.0444	0.1691	2.88 (0-01)
U(2)	0.5097	0.2500	-0.0755	Se(1)	0.4064	0.4556	0.1691	2.88 (0-01)
U(2)	0.4904	-0.2500	0.0755	Se(1)	0.4064	0.0444	0.1691	2.80 (0-01)
U(2)	0.4904	-0.2500	0.0755	Se(1)	0.4064	0.4556	0.1691	2.80 (0-01)

(b) Se-Se distances

Se(1)	0.4064	0.0444	0.1691	Se(2)	0.1874	0.2500	0.3328	3.47 (0.01)
Se(1)	0.4064	0.0444	0.1691	Se(3)	0.5003	0.2500	0.5387	3.56 (0.01)
Se(3)	0.5003	0.2500	0.5387	Se(4)	0.2842	0.2500	0.8074	3.40 (0.01)
Se(4)	0.2842	0.2500	0.8074	Se(1)	0.4064	0.0444	1.1691	3.64 (0.01)
Se(1)	0.4064	0.0444	0.1691	Se(1)	0.5936	-0.0444	-0.1691	3.59 (0.01)
Se(3)	0.5003	0.2500	0.5387	Se(1)	0.5936	-0.0444	0.8309	3.57 (0.01)
Se(4)	0.2842	0.2500	0.8074	Se(1)	0.0936	0.5444	0.6691	3.61 (0.01)
Se(1)	0.4064	0.0444	0.1691	Se(1)	0.4064	0.4556	0.1691	3.49 (0.01)

(c) U-U distances

U(2)	0.00965	0.25000	0.57548	U(1)	-0.17745	0.00007	0.97154	4.40 (0-0)
U(2)	0.00965	0.25000	0.57548	U(1)	-0.17745	0.49993	0.97154	4.40 (0-0)
U(1)	0.17745	0.99993	0.02846	U(1)	0.17745	0.50007	0.02846	4.24 (0-0)
U(1)	0.17745	0.99993	0.02846	U(1)	0.32255	1.00007	-0.47154	4.28 (0-0)

Table 5. Angles at selenium atoms ($^{\circ}$)
with standard deviations in parentheses

In Tables 5 and 6, and in Figs. 2 and 3, atoms are marked with superscripts to differentiate between equivalent positions.

U(1)—Se(1)—U(1^i)	89.7 (0.2)
U(1)—Se(1)—U(2^{ii})	104.6 (0.2)
U(1)—Se(1)—U(2^{iii})	98.2 (0.2)
U(1^{ii})—Se(1)—U(2^i)	147.5 (0.2)
U(1^{ii})—Se(1)—U(2^{ii})	105.0 (0.2)
U(2^{ii})—Se(1)—U(2^i)	101.7 (0.2)
U(1)—Se(2)—U(2)	117.0 (0.3)
U(1^{ii})—Se(2)—U(2)	117.0 (0.3)
U(1^i)—Se(2)—U(2)	95.4 (0.3)
U(1^{iii})—Se(2)—U(2)	95.4 (0.3)
U(1)—Se(2)—U(1^{ii})	83.7 (0.2)
U(1^i)—Se(2)—U(1^{ii})	86.3 (0.2)
U(1)—Se(2)—U(1^i)	86.0 (0.2)
U(1^{ii})—Se(2)—U(1^{ii})	86.0 (0.2)
U(1^i)—Se(3)—U(2^i)	93.1 (0.2)
U(1^{iii})—Se(3)—U(2^i)	93.1 (0.2)
U(1^{iv})—Se(3)—U(2^i)	98.1 (0.2)
U(1^v)—Se(3)—U(2^i)	98.1 (0.2)
U(1^i)—Se(3)—U(1^{iii})	86.3 (0.2)
U(1^{iv})—Se(3)—U(1^v)	87.6 (0.2)
U(1^i)—Se(3)—U(1^{iv})	92.0 (0.2)
U(1^{iii})—Se(3)—U(1^v)	92.0 (0.2)
U(1)—Se(4)—U(2^{ii})	94.0 (0.2)
U(1^{ii})—Se(4)—U(2^{ii})	94.0 (0.2)
U(1^i)—Se(4)—U(2^{ii})	104.0 (0.2)
U(1^{iii})—Se(4)—U(2^{ii})	104.0 (0.2)
U(1)—Se(4)—U(1^{ii})	87.4 (0.2)
U(1^i)—Se(4)—U(1^{ii})	88.7 (0.2)
U(1)—Se(4)—U(1^i)	89.1 (0.2)
U(1^{ii})—Se(4)—U(1^{ii})	89.1 (0.2)

Table 6. Least-squares best planes

Plane 1:		$-0.4366x - 0.6443y - 0.6279z + 6.826 = 0$		
Atoms in plane		X	Y	Z
U(1)	4.0093	4.2394	4.1061	-0.2337
Se(1)	1.1636	4.6167	5.1987	0.0796
Se(3)	6.2182	2.1200	4.1856	0.1173
Se(4)	3.5329	2.1200	6.2734	-0.0212
Se(4^i)	2.6821	6.3600	2.3884	0.0580
Atoms out of plane				
Se(2)	2.3298	2.1200	2.5856	2.8198
Se(1^i)	5.0514	3.8633	1.3138	1.3069
Se(2^i)	3.8852	6.3600	6.4706	-3.0306
Se(3^i)	6.2118	6.3600	3.5844	-2.2340
Plane 2:		$-0.6153x + 0.6496y - 0.4466z + 1.2766 = 0$		
Atoms in plane		X	Y	Z
U(1)	4.0093	4.2394	4.1061	-0.2701
Se(2)	2.3298	2.1200	2.5856	0.0655
Se(1^i)	5.0514	3.8633	1.3138	0.0915
Se(2^i)	3.8852	6.3600	6.4706	0.1277
Se(3^i)	6.2118	6.3600	3.5844	-0.0147
Atoms out of plane				
Se(1)	1.1636	4.6167	5.1987	1.2378
Se(3)	6.2182	2.1200	4.1856	-3.0415
Se(4)	3.5329	2.1200	6.2734	-2.3217
Se(4^i)	2.6821	6.3600	2.3884	2.6911

Dihedral angle between plane 1 and plane 2 = 82.5° .

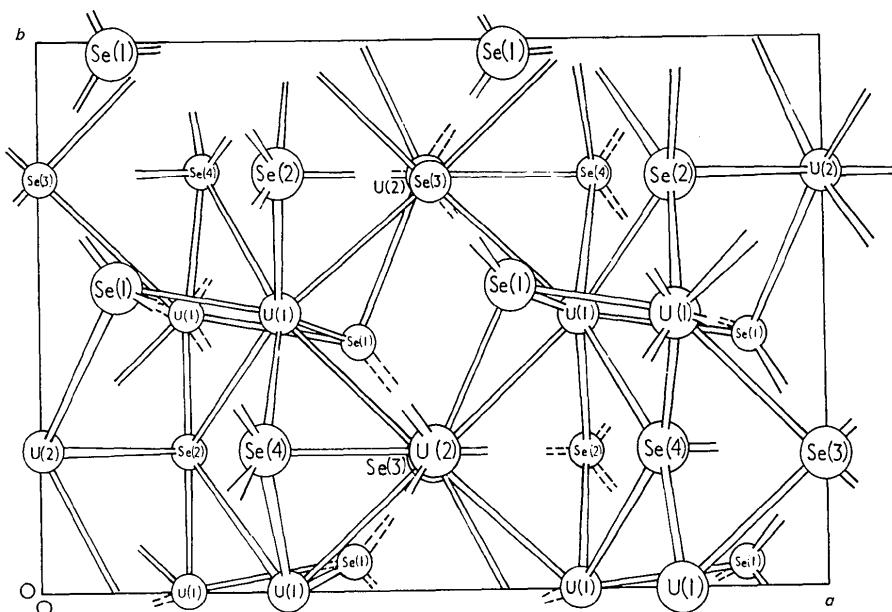


Fig. 1. View of the unit cell of U_3Se_5 down the [001] direction. Individual atoms may be identified by their fractional coordinates after reference to Table 4. Large circles correspond to atoms with z/c parameters approaching unity and small circles represent atoms with z/c near to zero.

will approach the ideal configurations which have been proposed for isolated polyhedra (King, 1970) and indeed the environments of the uranium atoms are far from regular. Fig. 2 shows the two sets of four atoms comprising the most obvious pair of intersecting trapezoids around U(1). The dihedral angle between the best planes through the trapezoids (82.5°) is intermediate between the values expected (Lippard & Russ, 1968) for a dodecahedral (90°) and an anti-prismatic (77.4°) arrangement. The environment around U(2), which is shown in Fig. 3, is also irregular.

Details of the least-squares planes calculated to elucidate the stereochemistry around U(1) are given in Table 6.

The arrangements of near-neighbour uranium atoms around Se(2), Se(3) and Se(4) are roughly square pyramidal although the deviations of some of the angles at Se(2) from the optimum are considerable. Table 5 also shows that the arrangement around Se(1) is somewhat removed from tetrahedral.

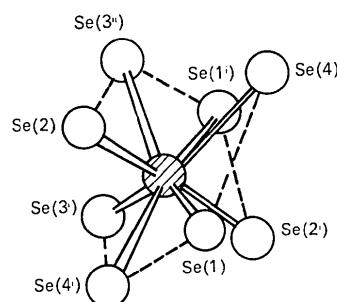


Fig. 2 The environment of U(1).

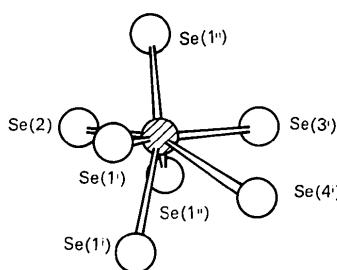


Fig. 3. The environment of U(2). Selenium atoms with identical superscripts are related by the mirror plane at $z=0.25$.

Since the length of any individual U–Se distance is clearly influenced by factors such as the coordination numbers of both atoms involved, a comparison of the mean separation at each of the uranium atoms with the sum of the octahedral ionic radii for U^{3+} (Peterson & Cunningham, 1968) and Se^{2-} (Pauling, 1960), and for U^{4+} (Peterson & Cunningham, 1967) and Se^{2-} (2.985 and 2.909 Å respectively) does not afford a simple criterion for establishing the charged species present in the crystal of U_3Se_5 . Nevertheless it will be noted that the approximate match between these values and the mean values for U(1) and U(2) quoted above, together with the 2:1 numerical ratio of the metal atom types, is consistent with the ionic composition $M^{4+}M^{3+}_2\text{Se}^{2-}_5$ which has been anticipated both for this crystal type (Marcon, 1967) and for the related materials $M_1(M_2)_2\text{Se}_5$ where M_1 and M_2 are different metals (Marcon & Pascard, 1968).

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