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The Crystal Structure of Triuranium Pentaselenide

BY P. T. MOSELEY

Applied Chemistry Division, A.E.R.E., Harwell, Berkshire, England

AND D. BROWN AND B. WHITTAKER

Chemistry Division, A.E.R.E., Harwell, Berkshire, England

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Triuranium pentaselenide, U_3Se_5 , crystallizes with an orthorhombic unit cell; $a_0 = 12.43$ (2), $b_0 = 8.48$ (1) and $c_0 = 7.77$ (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 $900^\circ C$ 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:

$$a_o = 12.43 \pm 0.02, \quad b_o = 8.48 \pm 0.01, \quad c_o = 7.77 \pm 0.01 \text{ \AA}$$

$0kl$ reflexions absent for $k+l$ odd
 $hk0$ reflexions absent for h odd.

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-

Table 1. Refinement in the alternative space groups
 Positional parameters ($\times 10^4$) and thermal parameters ($\times 10^3$). $B = 8\pi^2u$.

<i>Pna2₁</i>						
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)	
<i>Pnma</i> (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)	

* The authors are indebted to Mr K. L. Wilkinson of Applied Chemistry Division A.E.R.E., Harwell for the preparation of the crystals.

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 ⁱ)	104.6 (0.2)
U(1)—Se(1)—U(2 ⁱⁱⁱ)	98.2 (0.2)
U(1 ⁱ)—Se(1)—U(2 ⁱ)	147.5 (0.2)
U(1 ⁱ)—Se(1)—U(2 ⁱⁱⁱ)	105.0 (0.2)
U(2 ⁱⁱⁱ)—Se(1)—U(2 ⁱ)	101.7 (0.2)
U(1)—Se(2)—U(2)	117.0 (0.3)
U(1 ⁱⁱⁱ)—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 ⁱⁱⁱ)	83.7 (0.2)
U(1 ⁱ)—Se(2)—U(1 ⁱⁱⁱ)	86.3 (0.2)
U(1)—Se(2)—U(1 ⁱ)	86.0 (0.2)
U(1 ⁱⁱⁱ)—Se(2)—U(1 ⁱⁱⁱ)	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 ⁱⁱⁱ)—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 ⁱⁱⁱ)	87.4 (0.2)
U(1 ⁱ)—Se(4)—U(1 ⁱⁱⁱ)	88.7 (0.2)
U(1)—Se(4)—U(1 ⁱ)	89.1 (0.2)
U(1 ⁱⁱⁱ)—Se(4)—U(1 ⁱⁱⁱ)	89.1 (0.2)

Table 6. *Least-squares best planes*

Plane 1:				
$-0.4366x - 0.6443y - 0.6279z + 6.826 = 0$				
Atoms in plane	Coordinates (Å)			Distance from mean 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	Distance from mean plane
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°.

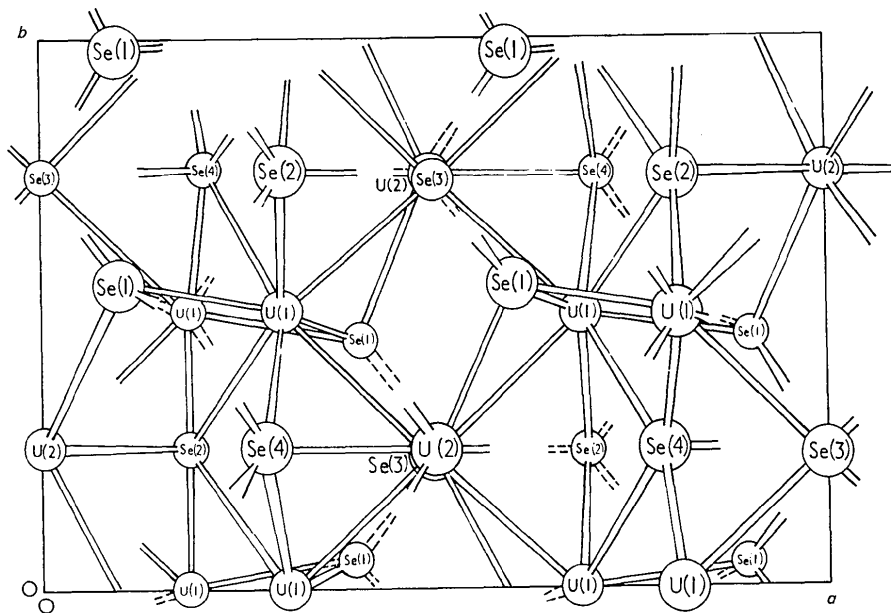


Fig. 1. View of the unit cell of U_3Se_5 down the [001] direction. Individual atoms may be identified by their fractional coordinates after reference to Table 4. Large circles correspond to atoms with z/c parameters approaching unity and small circles represent atoms with z/c near to zero.

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.

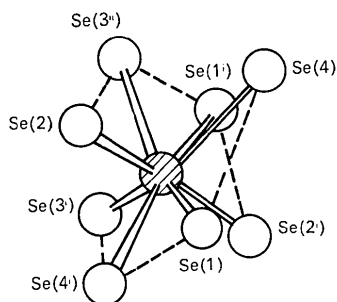


Fig. 2 The environment of U(1).

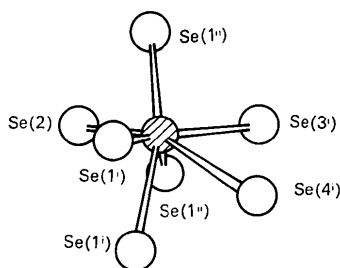


Fig. 3. The environment of U(2). Selenium atoms with identical superscripts are related by the mirror plane at $z=0.25$.

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 $M^{4+}M^{3+}_2Se_5^{2-}$ which has been anticipated both for this crystal type (Marcon, 1967) and for the related materials $M_1(M_2)_2Se_5$ where M_1 and M_2 are different metals (Marcon & Pascard, 1968).

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