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Acta Cryst. (1985). C**41**, 1571–1573

Structure of a Uranyl Diselenite, $UO_2Se_2O_5$

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(*Received* 28 *February* 1985; *accepted* 29 *July* 1985)

Abstract. $M_r = 508$, triclinic, $P\bar{1}$, $a = 9{\cdot}405\,(2)$, $b = 11{\cdot}574\,(2)$, $c = 6{\cdot}698\,(2)$ Å, $\alpha = 93{\cdot}01\,(3)$, $\beta = 93{\cdot}66\,(3)$, $\gamma = 109{\cdot}69\,(1)°$, $V = 683{\cdot}0\,(6)$ Å^3, $Z = 4$, $D_x = 4{\cdot}94$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 33{\cdot}1$ mm^{-1}, $F(000) = 864$, $T = 293$ K, final $R = 0{\cdot}030$ for 2177 observed reflections with $I > 3\sigma(I)$. The material was synthesized by gas–solid reaction around 720 K, using SeO_2 and UO_3. U, as uranyl cations UO_2^{2+}, is sevenfold coordinated. Two pentagonal bipyramids share one edge to form $[U_2O_{12}]$ entities, which are linked by [>Se—O—Se<] groups, giving rise to a lamellar structure with layers parallel to the (010) plane.

Introduction. Studies concerning selenites of transition elements are of particular interest because of: (i) the specific stereochemistry of the Se^{IV} element with the presence of a lone pair (Bertaud, 1974; Kohn, Inoue, Horie & Akimoto, 1976; Meunier, Bertaud & Galy, 1974); (ii) the specific architecture of some of these compounds, which exhibit a low-dimensional character. Both features must sometimes be considered to account for the interesting properties of selenites, *e.g.* magnetism in the case of $CuSe_2O_5$ (Kahn, Verdaguer, Girerd, Galy & Maury, 1980) or $VOSeO_3$ (Gleizes, Trombe, Enjalbert, Galy, Journeaux & Verdaguer, 1983).

Uranyl selenites were first synthesized a century ago, but their characterization was carried out more recently by Claude (1960*a*,*b*) who described various phases such as $UO_2Se_2O_5$, UO_2SeO_3,.... The thermal behaviour of some of these phases was re-examined (Khandelwal & Verma, 1976) and the structure of UO_2SeO_3 was determined by Loopstra & Brandenburg (1978) by using neutron powder data. In the course of our study concerning transition-element selenites, $UO_2Se_2O_5$ was prepared and its structure is reported here.

Experimental. Pale-yellow single crystals grown from reaction, around 720 K, in sealed tube, of a mixture UO_3–$2SeO_2$ (reagent grade, dried before the run) with excess SeO_2: this excess removed by further heating around 470 K. Chemical analyses, U = 46·3, Se = 31·4 wt% in agreement with $UO_2Se_2O_5$. Preliminary study–precession camera (Mo $K\alpha$)–on single crystal, 0·05 × 0·035 × 0·29 mm, bounded by (010), (110) and (001) planes, indicated triclinic system. CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$; cell parameters from least-squares fit of setting angles of 25 reflections with 2θ between 6·9 and 41·5°; 2289 non-zero reflections measured using ω–θ scan for 2θ values 3 to 52° ($h = -11$ to 11, $k = -14$ to 14, $l = 0$ to 8), scan range $1{\cdot}05° + 0{\cdot}347°\tan\theta$; intensities of three reflections ($\bar{3}11$, $\bar{1}41$, $\bar{1}\bar{1}4$), measured every 3600 s during data collection, varied <2%; corrections for Lp and for absorption (transmission factors max. = 0·414, min. = 0·192); structure determination in space group $P\bar{1}$ by heavy-atom method followed by Fourier and least-squares techniques using 2177 reflections with $I > 3\sigma(I)$, full matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ with anisotropic thermal parameters for all atoms, $R = 0{\cdot}030$ and $wR = 0{\cdot}060$,*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42408 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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182 variables; $w = 0{\cdot}58[\sigma^2(F_o) + 3 \times 10^{-4} F_o^2]^{-1}$, $S = 1{\cdot}16$, max. Δ/σ in final refinement cycle = 0·07, max. and min. heights in final ΔF map 3·28 and −3·41 e Å^{-3}, secondary-extinction factor 3×10^{-4}; scattering factors including real and imaginary parts of anomalous dispersion from *International Tables for X-ray Crystallography* (1974), *SHELX*76 (Sheldrick, 1976) and *ORFFE* (Busing, Martin & Levy, 1964) programs.

Discussion. The final positional and equivalent isotropic thermal parameters are listed in Table 1 and bond lengths and angles in Table 2. Both U(1) and U(2) form uranyl groups UO_2^{2+}, characterized by the presence of short U—O bonds, average 1·770 Å (Wells, 1962). The uranium atom coordination is seven and the coordination polyhedra can be represented as pentagonal bipyramids (Fig. 1); this coordination and polyhedron shape frequently occur for uranyl groups (Legros, 1976; Shchelokov, Mikhailov, Orlova, Sergeev, Beyrahov, Kanishcheva & Lobanova, 1983; Meunier & Galy, 1973). As usual, the equatorial bonds of the pentagonal bipyramids are longer than the axial ones: they range from 2·33 to 2·50 Å (Table 2). The uranium atoms and their five neighbouring equatorial oxygen atoms are approximately planar, as can be seen from the sum of the angles O—U—O (Table 2): the maximum deviations from the least-squares planes are 0·053 (8) Å in the case of the U(1)–oxygen plane and 0·033 (8) Å for the U(2)–oxygen plane.

The two pentagonal bipyramids are joined by an edge, O(5)–O(6), thus forming an original dinuclear entity $[U_2O_{12}]$ with a uranium–uranium distance of 4·079 (1) Å (Fig. 1). The dihedral angle between the equatorial planes of each pentagonal bipyramid is 27·2 (1)°. The presence of a common edge for the two pentagonal bipyramids explains the disparity between the uranium–oxygen equatorial bond lengths. For both uranium atoms the distances U—O(5) and U—O(6) are significantly larger than the other U—O distances, and the angles O(5)—U—O(6) are smaller than the other O—U—O angles (Table 2). Since the O(5)—O(6) distance is also short, *i.e.* O(5)—O(6) = 2·62 (1) Å, such a situation can be directly related to the strong electrostatic repulsion occurring between the highly charged uranium atoms.

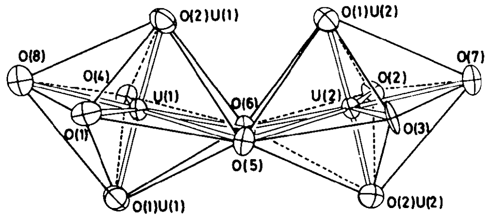

Fig. 1. *ORTEP* (Johnson, 1965) representation of the uranium dinuclear entities (U_2O_{12}).

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å^2 × 10^2) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
U(1)	0·04809 (4)	0·23878 (4)	0·42399 (6)	1·27 (2)
U(2)	−0·34626 (4)	0·23981 (4)	0·13409 (6)	1·28 (2)
Se(1)	0·0409 (1)	0·3454 (1)	0·9308 (2)	1·47 (5)
Se(2)	−0·2489 (1)	0·3461 (1)	0·6578 (2)	1·55 (5)
Se(3)	0·2363 (1)	0·1174 (1)	0·0380 (2)	1·93 (5)
Se(4)	0·3650 (1)	0·1185 (1)	0·4888 (2)	2·11 (6)
O(1U1)	0·1540 (9)	0·3969 (8)	0·477 (1)	2·6 (5)
O(2U1)	−0·0649 (9)	0·0826 (7)	0·366 (1)	2·3 (4)
O(1U2)	−0·3684 (9)	0·0832 (8)	0·157 (1)	2·7 (5)
O(2U2)	−0·3170 (9)	0·3980 (8)	0·115 (1)	2·9 (5)
O(Se1)	−0·0704 (8)	0·4246 (7)	0·806 (1)	1·8 (4)
O(Se3)	0·2675 (9)	0·0384 (8)	0·253 (1)	2·7 (5)
O(1)	0·1927 (8)	0·2328 (7)	0·154 (1)	1·9 (4)
O(2)	−0·4964 (8)	0·2349 (7)	0·405 (1)	1·7 (4)
O(3)	−0·3172 (8)	0·2248 (7)	−0·212 (1)	1·8 (4)
O(4)	0·0093 (8)	0·2262 (7)	0·765 (1)	1·9 (4)
O(5)	−0·0743 (8)	0·2819 (7)	0·111 (1)	1·7 (4)
O(6)	−0·1848 (8)	0·2880 (7)	0·459 (1)	1·7 (4)
O(7)	−0·5904 (9)	0·1873 (8)	−0·021 (1)	2·6 (4)
O(8)	0·2503 (8)	0·1879 (8)	0·568 (1)	2·1 (4)

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Around uranium atoms			
U(1)–O(1U1)	1·768 (8)	U(2)–O(1U2)	1·770 (9)
U(1)–O(2U1)	1·769 (7)	U(2)–O(2U2)	1·770 (9)
U(1)–O(1)	2·347 (7)	U(2)–O(2)	2·363 (7)
U(1)–O(4)	2·338 (7)	U(2)–O(3)	2·358 (7)
U(1)–O(5)	2·480 (7)	U(2)–O(5)	2·454 (7)
U(1)–O(6)	2·463 (8)	U(2)–O(6)	2·495 (7)
U(1)–O(8)	2·339 (9)	U(2)–O(7)	2·326 (8)
O(1U1)–U(1)–O(2U1)	177·3 (4)	O(1U2)–U(2)–O(2U2)	177·8 (4)
O(1)–U(1)–O(5)	69·6 (3)	O(2)–U(2)–O(7)	76·5 (3)
O(5)–U(1)–O(6)	63·9 (2)	O(7)–U(2)–O(3)	75·1 (3)
O(6)–U(1)–O(4)	75·2 (3)	O(3)–U(2)–O(5)	74·8 (2)
O(4)–U(1)–O(8)	74·8 (3)	O(5)–U(2)–O(6)	63·8 (2)
O(8)–U(1)–O(1)	76·5 (3)	O(6)–U(2)–O(2)	69·7 (2)
	$\sum$360·0		$\sum$359·9
Around selenium atoms			
Se(1)–O(4)	1·658 (8)	O(4)–Se(1)–O(5^{i})	102·2 (4)
Se(1)–O(5^{i})	1·703 (7)	O(5^{i})–Se(1)–O(Se1)	100·1 (4)
Se(1)–O(Se1)	1·802 (9)	O(Se1)–Se(1)–O(4)	100·0 (4)
Se(2)–O(3^{i})	1·654 (8)	O(3^{i})–Se(2)–O(6)	102·7 (4)
Se(2)–O(6)	1·696 (8)	O(6)–Se(2)–O(Se1)	99·9 (3)
Se(2)–O(Se1)	1·816 (7)	O(Se1)–Se(2)–O(3^{i})	100·0 (3)
Se(3)–O(1)	1·688 (9)	O(1)–Se(3)–O(7^{ii})	102·8 (4)
Se(3)–O(7^{ii})	1·642 (8)	O(7^{ii})–Se(3)–O(Se3)	102·3 (4)
Se(3)–O(Se3)	1·808 (9)	O(Se3)–Se(3)–O(1)	994·4 (4)
Se(4)–O(2^{ii})	1·678 (7)	O(2^{ii})–Se(4)–O(8)	102·1 (4)
Se(4)–O(8)	1·644 (9)	O(8)–Se(4)–O(Se3)	102·9 (4)
Se(4)–O(Se3)	1·810 (8)	O(Se3)–Se(4)–O(2^{ii})	100·6 (3)
Intralayer van der Vaals contacts			
Se(1)–O(1^{i})	2·674 (8)		
Se(2)–O(2)	2·680 (6)		

Symmetry codes: (i) $x, y, 1 + z$; (ii) $1 + x, y, z$.

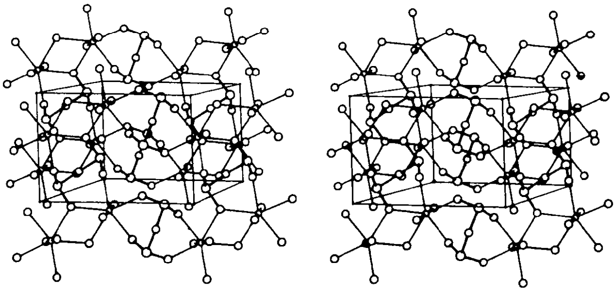

Fig. 2. Stereoscopic view of the $UO_2Se_2O_5$ structure; *a* horizontal, *c* vertical.

Two sets of diselenite groups $[Se_2O_5]$ per asymmetric unit (Table 2) are observed. The O—Se distances and angles may be compared for these two groups, which are characterized by two short bonds between 1·64 and 1·70 Å and a longer one around 1·80 Å; this latter occurs in the [Se—O—Se] bridge (Meunier & Galy, 1973). The O—Se—O angles range from 100 to 103° (Table 2); such values are characteristic of the particular stereochemistry of Se^{IV} with an active lone pair: the Se atom can be considered as located inside a trigonal pyramid, with the lone pair at the apex and the three bound oxygen atoms constituting the trigonal base (Galy, Meunier, Andersson & Aström, 1975).

The diselenite ligands, represented by $[Se_2O]$, link the uranium dinuclear entities $[U_2O_{12}]$ (Fig. 2). The first diselenite group Se(1)—O(Se1)—Se(2) bridges the dinuclear entities along the [100] direction, while the second Se(3)—O(Se3)—Se(4) plays a similar role in the [001] direction, giving rise to layers parallel to the (010) plane (Fig. 2). Thus, the $UO_2Se_2O_5$ lattice can be described as a lamellar lattice exhibiting marked two-dimensional character. No specific van der Waals contacts appear between two consecutive layers (Table 2). The weak interlayer cohesion may account for the crystal fragility.

One of us (JCT) is particularly indebted to Miss F. Dahan and M J. M. Savariault for their kind assistance during the structure calculation.

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Acta Cryst. (1985). C**41**, 1573–1575

$Zn_2Ti_{18}S_{32}$, a New Ternary Sulfide

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(*Received* 8 *January* 1985; *accepted* 22 *April* 1985)

Abstract. $M_r = 2019{\cdot}07$, cubic, $Fd3m$, $a = 9{\cdot}843\,(1)$ Å, $V = 953{\cdot}64$ Å^3, $Z = 1$, $D_m = 3{\cdot}51\,(2)$, $D_x = 3{\cdot}515$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5405$ Å, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu(\text{Cu } K\alpha) = 48{\cdot}42$ mm^{-1}, $\mu(\text{Mo } K\alpha) = 6{\cdot}59$ mm^{-1}, $F(000) = 968$, room temperature, $R = 0{\cdot}0695$ for 67 reflections from powder diffraction data.

0108-2701/85/111573-03$01.50