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Chemistry, Crystal Structure, and Structural Evolution versus Temperature of the Uranyl Diselenite $UO_2Se_2O_5$: Structural Relationships with $(UO_2)Se_2O_5 \cdot 2H_2O$, UO_2SeO_3, and β-U_3O_8

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The chemistry and structural chemistry versus temperature in the system UO_3–SeO_2–H_2O were determined. A proposal has been presented for the structural transformations of various selenites, i.e., $UO_2Se_2O_5 \cdot 2H_2O$, $UO_2Se_2O_5$, UO_2SeO_3, and the U_3O_8 uranium oxide final product in its β form. The unit-cell of the hydrated uranyl diselenite has been determined from an indexed powder pattern: it crystallizes in the triclinic system with $a = 9.40(4)$ Å, $b = 11.85(5)$ Å, $c = 6.69(5)$ Å, $\alpha = 94.3(3)°$, $\beta = 90.3(3)°$, and $\gamma = 114.5(3)°$, $V = 676$ Å^3. On this basis, a structure derived from that of $UO_2Se_2O_5$ is proposed, corresponding to a reasonable packing of oxygen, water molecules, and lone pairs.

Introduction

Inner transition element selenites, both lanthanides and actinides have been less studied than those of the corresponding *d* transition elements. However, because of the importance of uranium, some effort has been particularly devoted to this element. The discovery of uranyl selenites dates back to the last century (*1*), but their synthesis was only precisely described some 20 years ago, particularly by Claude (*2*) who prepared several uranyl selenites and characterized them by their thermal behavior and X-ray powder diagrams. The thermal evolution of the simple uranyl selenites can be described as (*2, 3*)

$$UO_3 \cdot 2SeO_2 \cdot 2H_2O \xrightarrow{150\text{–}200°C} UO_2Se_2O_5 + 2H_2O(g) \quad \text{(I)}$$

$$UO_2Se_2O_5 \xrightarrow{290\text{–}350°C} UO_2SeO_3 + SeO_2(g) \quad \text{(II)}$$

$$3UO_2SeO_3 \xrightarrow{550\text{–}670°C} U_3O_8 + 3SeO_2(g) + \tfrac{1}{2}O_2(g) \quad \text{(III)}$$

The synthesis of simple uranyl selenites as above, through the thermal decomposition at atmospheric pressure of such complex salts as $(NH_4)_2(UO_2)_2(SeO_3)_3(H_2O)_6$ has been more recently reinvestigated (*4*). The observed results (*4*) quite agree with the previous ones (*2*). The enthalpy of formation of UO_2SeO_3 has been determined (*5*) and its structure has been solved recently from X-ray and neutron diffraction powder data (*6*).

As part of our program concerning low dimensional compounds with unusual physical properties, the uranyl diselenite, $UO_2Se_2O_5$, has been prepared as single

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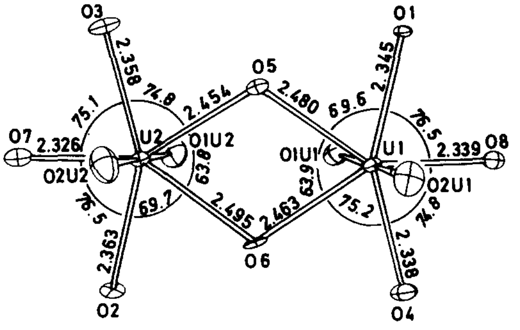


FIG. 1. $[U_2O_{12}]$ units formed by edge sharing of two pentagonal bipyramids $[UO_7]$.

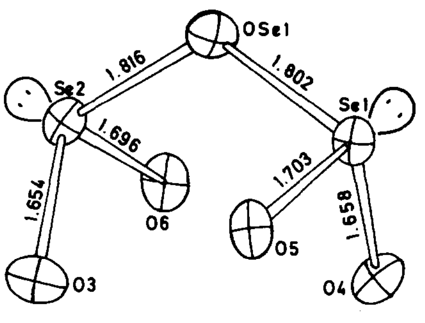


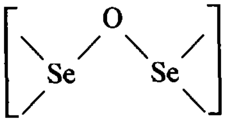
FIG. 2. The bisbidentate diselenite ligand $Se_2O_5^{2-}$.

crystal, and its structure determined and reported elsewhere (7). The aim of the present paper is (i) to recall briefly the main features of this structure and (ii) in the light of this structural information and of the scheme of thermal decomposition quoted above (Eqs. (I) to (III)) to propose a possible structure for the related compound, $UO_3{\cdot}2SeO_2{\cdot}2H_2O$, as well as for the transformation of $UO_2Se_2O_5$ to UO_2SeO_3 and U_3O_8.

Results and Discussion

1. Structure of $UO_2Se_2O_5$

$UO_2Se_2O_5$ crystallizes in the triclinic system, space group $P\bar{1}$ with a = 9.405(2) Å, b = 11.574(2) Å, c = 6.698(2) Å, α = 93.01(1)°, β = 93.66(9)°, γ = 109.69(1)°, V = 683 Å^3, Z = 4. It contains $[U_2O_{12}]$ units formed by two pentagonal bipyramids with a common edge (Fig. 1). The bisbidentate diselenite groups



or $[Se_2O_5]^{2-}$ (Fig. 2) bridge these dinuclear entities along the [100] and [001] directions, giving rise to a lamellar lattice, with layers parallel to the (010) plane (Fig. 3). The cohesion between the layers must be weak

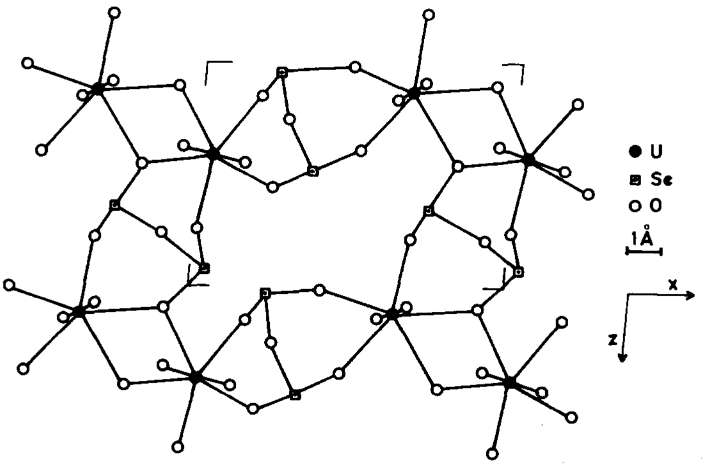


FIG. 3. Projection onto the plane (010) of one $[UO_2Se_2O_5]$ layer.

TABLE I

INDEXED POWDER DIAGRAM OF $UO_2Se_2O_5$

h k l	d_{obs}	d_{calcd}	I/I_0 calcd (13)	*d*(2)	*h k l*	d_{obs}	d_{calcd}	I/I_0 calcd (13)	*d*(2)
0 1 0	10.83	10.86	9		1 2 2	2.46	2.46	11	2.50
1 0 0	8.76	8.82	21		2 $\bar{3}$ 2	2.40	2.40	3	2.43
1 $\bar{1}$ 0	8.44	8.39	26						2.37
				6.28	3 $\bar{4}$ $\bar{1}$	2.30	2.31	1	
1 0 $\bar{1}$		5.55	10		3 $\bar{4}$ 1		2.31	<1	
1 $\bar{2}$ 0		5.55	4		1 $\bar{5}$ 0		2.30	<1	
0 1 1		5.49	9		3 $\bar{2}$ 2	2.20	2.20	2	2.24
0 2 0	5.43	5.43	100		3 $\bar{1}$ $\bar{2}$		2.20	2	
1 $\bar{1}$ 1	5.13	5.18	9	5.18	1 4 1	2.17	2.18	3	
1 0 1		5.11	6		0 5 0		2.17	<1	
				4.93	4 $\bar{2}$ 1		2.17	<1	
2 $\bar{1}$ 0	4.68	4.68	15	4.66	1 $\bar{5}$ $\bar{1}$	2.13	2.13	6	2.10
				4.44	3 $\bar{3}$ 2		2.12	3	
1 1 1	4.22	4.22	4		2 $\bar{3}$ 2	2.06	2.06	2	2.07
1 $\bar{2}$ 1		4.21	8		2 $\bar{2}$ 3	1.979	1.981	2	1.97
2 $\bar{2}$ 0		4.20	6		3 $\bar{4}$ $\bar{2}$		1.978	2	1.95
1 $\bar{3}$ 0	3.86	3.84	14	3.86	2 0 3	1.914	1.918	1	1.92
2 1 0	3.66	3.67	18		4 0 $\bar{2}$		1.917	3	
1 2 $\bar{1}$	3.61	3.62	19		3 $\bar{1}$ $\bar{3}$	1.873	1.872	1	
2 0 1	3.53	3.54	15	3.54	1 2 3		1.871	2	1.90
2 2 1		3.52	16	3.52	2 2 $\bar{3}$		1.871	1	
2 $\bar{3}$ 0	3.43	3.45	13	3.46	2 $\bar{3}$ $\bar{3}$	1.860	1.859	2	
0 0 2	3.33	3.33	7	3.36	3 3 1	1.845	1.844	1	
1 2 1		3.32	2		5 $\bar{1}$ 0		1.844	5	
1 $\bar{1}$ $\bar{2}$	3.11	3.12	25	3.18	0 6 0	1.809	1.810	3	1.81
3 $\bar{1}$ 0		3.12	4		3 $\bar{5}$ 2		1.806	1	
3 $\bar{2}$ 0	3.07	3.06	20		5 $\bar{3}$ 1	1.764	1.764	1	1.76
2 3 $\bar{1}$		3.06	5		5 0 $\bar{1}$	1.744	1.743	1	1.74
3 0 0	2.93	2.94	16	2.99	3 $\bar{3}$ 3	1.719	1.722	<1	1.70
3 $\bar{3}$ 0	2.80	2.80	3	2.82	4 $\bar{6}$ 0		1.716	1	
2 $\bar{1}$ $\bar{2}$		2.79	9		5 $\bar{1}$ $\bar{2}$	1.667	1.669	2	
0 4 0	2.72	2.72	2		0 1 $\bar{4}$		1.666	1	
2 $\bar{1}$ 2	2.64	2.64	14		1 1 $\bar{4}$	1.647	1.648	3	
2 $\bar{2}$ $\bar{2}$		2.63	7		3 $\bar{4}$ 3		1.647	3	
3 $\bar{3}$ 1	2.60	2.60	4		0 2 $\bar{4}$	1.629	1.629	3	
2 1 $\bar{2}$		2.60	8	2.58	0 1 4		1.628	3	
1 $\bar{4}$ $\bar{1}$		2.60	6		0 7 0	1.550	1.552	1	1.57

and no marked van der Waals contacts have been observed between oxygen and/or selenium atoms of two successive layers (*7*).

The X-ray powder diagram of $UO_2Se_2O_5$ is reported in Table I with all observed diffraction lines indexed on the basis of the crystallographic constants determined from the single crystal. The observed *d*-spacings are in good agreement with the values previously attributed to this phase by Claude (*2*), but some extra lines appear on his list and it is likely that the uranyl diselenite he observed was not quite pure (*2*).

2. *Transformation of $UO_3{\cdot}2SeO_2{\cdot}2H_2O$ in $UO_2Se_2O_5$*

Proposal for the crystal structure of the hydrated diselenite. As indicated above (Eq. (I)), $UO_2Se_2O_5$ is easily obtained by

TABLE II

INDEXED POWDER DIAGRAM OF $UO_2Se_2O_5 \cdot 2H_2O$

d in Ref. (2)	I/I_0 in Ref. (2)	$h\ k\ l$ proposed	d_{calcd}
5.45	60	0 1 1	5.46
5.32	100	0 2 0	5.37
5.15	20	1 0 1	5.16
4.75	20	$2\ \bar{1}\ 0$	4.70
3.54	20	2 0 1	3.53
3.34	20	0 0 2	3.33
3.08	60	$1\ \bar{1}\ \bar{2}$ 1 0 2	3.08 3.06
2.96	20	$1\ 1\ \bar{2}$ $1\ \bar{2}\ 2$	2.96 2.97
2.91	60	1 3 0	2.90
2.80	20	$1\ \bar{2}\ \bar{2}$ $3\ \bar{2}\ \bar{1}$	2.87 2.87
2.64	60	$3\ \bar{3}\ \bar{1}$	2.63
2.12	60	3 0 2 $0\ 2\ \bar{3}$ 1 4 1	2.12 2.12 2.12

the thermal decomposition of $UO_3 \cdot 2SeO_2 \cdot 2H_2O$ around 150°C (2). The latter compound can be reasonably postulated as $UO_2Se_2O_5 \cdot 2H_2O$, consisting, in essence, of the layered $UO_2Se_2O_5$ structure with intercalated water molecules between the layers. Such intercalated structures are well known and the guest molecules are usually easily removed by gentle heating.

With this assumption of the similarities of the two networks, the X-ray powder diagram of the hydrated compound was tentatively indexed on the basis of the d-spacings proposed by Claude (Table II) (2). All the observed lines can be indexed with the following refined constants $a = 9.40(4)$ Å, $b = 11.85(5)$ Å, $c = 6.69(5)$ Å, $\alpha = 94.3(3)°$, $\beta = 90.3(3)°$, $\gamma = 114.5(3)°$, $V = 676$ Å^3, the reliability factor[1] being 0.0031 (8). As expected, there are practically no changes of the a and c parameters, but a small increase of the b parameters, and some slight modifications of the angles, even the β angle, are observed. What seems more surprising is the constancy or even small decrease of the unit-cell volume with the intercalation of water. However, an explanation can be proposed in terms of (a) hydrogen bonding and (b) the volume occupied by the oxygen atoms and the selenium atoms with their lone pair E. As it has been shown, the volume of the lone pair is roughly comparable to that of an oxygen atom (9). The comparison of several diselenites of transition elements indicate that the mean volume (O + E) ranges from 15 to 16 Å^3 (Table III), the only exception being the anhydrous uranyl diselenite, which appears as a "loose" structure. In the counterpart the value obtained for the hydrated compound quite agrees with those of the other diselenites. It is therefore possible to account for the water of intercalation with only a small swelling of the interlayers constant, b, and with no overall change of volume. The slight modifications observed, either inside a layer or between the layers, displacement of two consecutive layers with respect to one another, apparently allow for a better stability of the lattice.

3. *Transformation of $UO_2Se_2O_5$ into UO_2SeO_3*

The decomposition of the diselenite, with SeO_2 loss (Eq. (II)), and the building principles to form the UO_2SeO_3 network may proceed as represented in Fig. 4 with the final structure being that proposed by Loopstra and Brandenburg (6).

A schematic representation of the

TABLE III

UNIT CELL VOLUMES AND AVERAGE O AND E VOLUMES IN SEVERAL DISELENITES

Diselenite	Unit-cell volume (Å^3)	Z	Mean volume (O,E)
$ZnSe_2O_5$ (14)	429.4	4	15.3
$VOSe_2O_5$ (15)	989.5	8	15.5
$CuSe_2O_5$ (16)	443.3	4	15.8
$TiOSe_2O_5$ (17)	247.6	2	15.5
$UO_2Se_2O_5$ (7)	683.0	4	19.0
$UO_2Se_2O_5 \cdot 2H_2O$	676	4	15.4

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[1] $R = [\Sigma(\theta_{obs} - \theta_{calcd})^2/\Sigma\theta^2_{obs}]^{1/2}$.

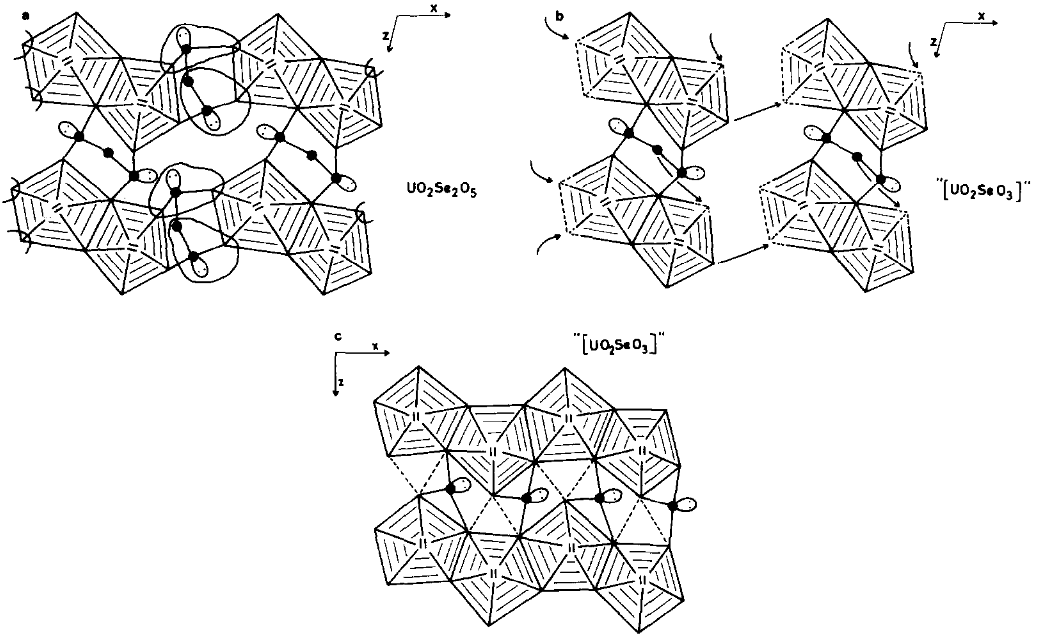
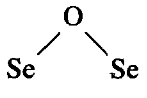


FIG. 4. Structural evolution from $UO_2Se_2O_5$ to UO_2SeO_3 after SeO_2 loss. (a) Breaking of the $Se_2O_5^{2-}$ groups bridging the $[U_2O_{12}]$ units along the [100] direction and loss of SeO_2 molecules. (b) "Intermediate" schematic structure. (c) "Resulting" UO_2SeO_3 structure, after breaking of the Se_2O_5 groups bridging the $[U_2O_{12}]$ units along the [001] direction and reorganization of the network. This structure is quasiisostructural with UO_2TeO_3 (*6, 10*).

$UO_2Se_2O_5$ starting structure with the $[U_2O_{12}]$ or, more precisely, $[(UO_2)_2O_8]$ units bridged by the $[Se_2O]$ bisbidentate groups is shown in Fig. 4a. The decomposition which requires the loss of SeO_2 (Eq. (II)), rather volatile at 300°C, most probably breaks the $[Se_2O_5]$ diselenite ligand. It is proposed that the desintegration starts in a plane parallel to (100) containing the diselenite groups linking the $[(UO_2)_2O_8]$ entities along the (100) direction; the atoms to be removed from the lattice, i.e., SeO_2 molecules (Eq. (II)) are encircled in Fig. 4a.

Subsequently, an "intermediate state" is assumed to be formed as illustrated by Fig. 4b. The second type of selenite groups bridging the $[(UO_2)_2O_8]$ units along the (001) axis will then break. The oxygen atoms of the



bridges participate in the network building after the structure has sheared by $\sim\frac{1}{3}[2\ 0\ \bar{1}]$ (100). After such an operation, one obtains a possible structure of UO_2SeO_3 (Fig. 4c). This postulated structure closely resembles that of UO_2TeO_3, first determined by Meunier and Galy (*10*) and then refined by Loopstra and Brandenburg (*6*). Only a

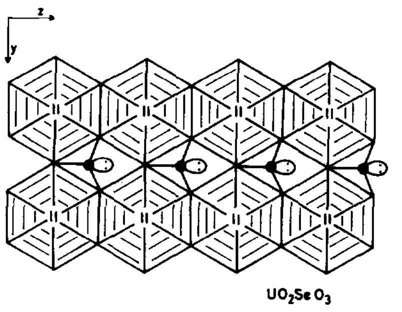


FIG. 5. The UO_2SeO_3 schematic representation according to Loopstra and Brandenburg (*6*).

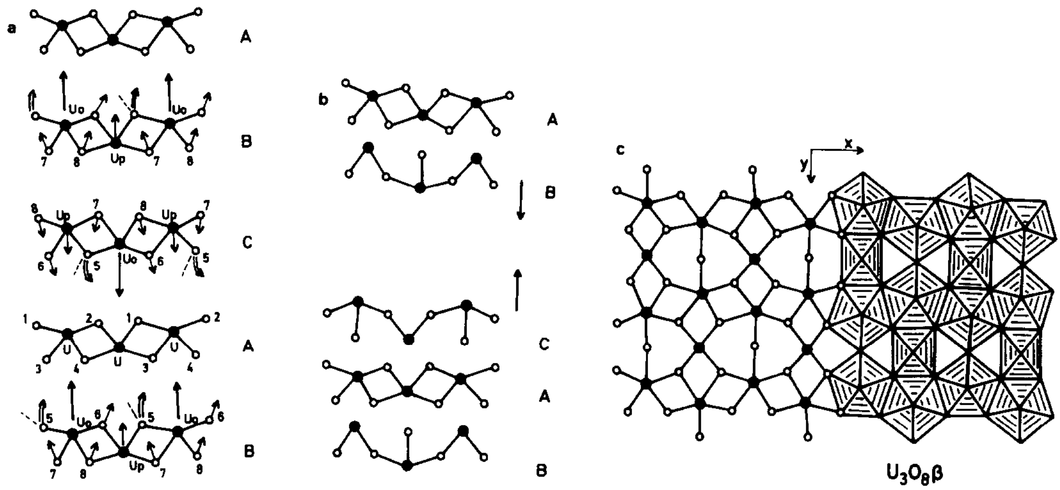


FIG. 6. Schematic illustration for the proposed structural evolution and rebuilding processes, resulting from the thermal decomposition of UO_2SeO_3 to β-U_3O_8. (a) Situation after the departure of the last SeO_2 groups; the arrows indicate the cooperative displacements of the various atoms to the anions position. (b) "Resulting" situation, the oxygen 5 having been lost. (c) The structure collapses and gives rise to the formation of the U_3O_8 crystalline network.

slight rearrangement of the network is needed to arrive at the actual structure of UO_2SeO_3 (Fig. 5) with uranium atoms in hexagonal bipyramids, sharing edges and corners of the equatorial plane (*6*). The selenium atom has the classical threefold coordination, with the lone pair at the apex of the SeO_3E pyramid. The structure is again lamellar, the $[UO_2SeO_3]_n$ layers stacking along the direction of the uranyl groups.

4. A proposal for the Transformation of UO_2SeO_3 into β-U_3O_8

It is of interest to recall that β-U_3O_8 has a tridimensional structure characterized by $[UO_7]$ pentagonal bipyramids (PBP) which share edges and corners, including the capping corners, and which encapsulate uranium atoms in octahedra $[UO_6]$ (Fig. 6) (*11*). There are two uranium atoms in PBP (U_p) for one in octahedra (U_o). To propose a scheme for the decomposition mechanisms, it is conceivable to do so over a sequence of six uranium atoms, pertaining to the $[UO_5]_n$ layers A, B, and C starting with the "intermediate" structure of UO_2SeO_3, i.e., Fig. 4c.

When the temperature increases to approximately 600°C (Eq. (III)) the remaining selenium atoms are lost as SeO_2 molecules. The resulting situation is presented on Fig. 6a assuming that the selenium atoms have taken out two oxygen atoms of the pentagonal base but that one oxygen atom of the uranyl group is shifted from its initial position toward the place left vacant by one of the oxygen atoms removed; the sequence ...O–U–O...O–U–O... of $UO_2Se_2O_5$ or of UO_2SeO_3 then becoming ...O–U–O–U–O... (Fig. 7). The rebuilding of the network goes on with a cooperative displacement of U_o toward oxygen atoms 1–2, and of the oxygen couples 8–6 and 7–5 and uranium atoms U_p toward the uranium atoms of the reference layer A (Fig. 6a). After such displacement, the oxygen atoms 5 of the layers B and C are eliminated, giving a step illustrated in Fig. 6b. In a last step the structure collapses (planes B – C) and the resulting structure, i.e., β-U_3O_8, is obtained (Fig. 6c).

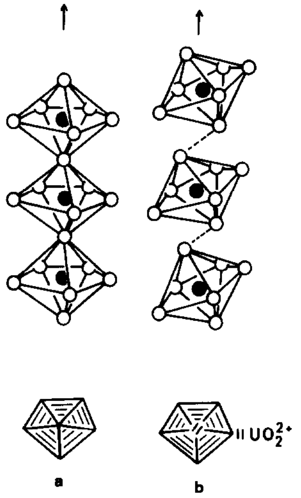


FIG. 7. Schematic representation of infinite strings: (a) of pentagonal bipyramids sharing corners, (b) of isolated pentagonal bipyramids piled up along a given direction.

The aim of this paper was to formulate the chemistry of the uranium selenites and to understand the phenomena giving a final product, β-U_3O_8, which is a reduced uranium oxide. As it has been shown, SeO_2 behaves like the other lone pair element oxides which act very often as "cutters" of transition oxide crystalline networks (*12*). The soft chemistry developed here, using gentle heating conditions, has allowed us to propose a mechanism of destroying and rebuilding the crystalline networks and has provided us with a reasonable structure for the hydrated diselenite, $UO_2Se_2O_5 \cdot 2H_2O$, in agreement with its X-ray powder pattern.

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