# Low-Temperature Crystal Structures and Thermal Decomposition of Uranyl Hydrogen Selenite Monohydrate, UO₂(HSeO₃)₂·H₂O and Diammonium Uranyl Selenite Hemihydrate, (NH₄)₂UO₂(SeO₃)₂·0.5H₂O

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The structures of the uranyl hydrogen selenite monohydrate, UO₂(HSeO₃)₂·H₂O and diammonium uranyl selenite hemihydrate, (NH₄)₂UO₂(SeO₃)₂·0.5H₂O have been determined by X-ray diffraction at 193 K and their thermal decomposition studied. The structure of (NH₄)₂UO₂(SeO₃)₂·0.5H₂O is layered. The layers are formed by the two unequal selenite ions acting as bridging ligands between three and two U^VI ions, respectively. The ammonium ions and the water molecule form an array, which through a complex hydrogen bond network holds the layers together. In UO₂(HSeO₃)₂·H₂O the hydrogen selenite ion acts as a bridging ligand between two consecutive U^VI ions, leading to a structure of one-dimensional zigzag chains. (NH₄)₂UO₂(SeO₃)₂·0.5H₂O decomposes in air between 570 and 640 K in a single thermogravimetric step to a phase containing uranyl selenite with additional selenium dioxide. The final product, U₃O₈, is formed between 870 and 930 K. After dehydration UO₂(HSeO₃)₂·H₂O decomposes to stoichiometric UO₂SeO₃·SeO₂. This compound decomposes further to the same non-stoichiometric uranyl selenite–selenium dioxide phase as the ammonium compound.

Dioxouranium(VI) or uranyl UO₂²⁺ ion is known to form several different selenium(IV) oxo compounds, but the structural characterisation of these has been scarce.[1] Only the crystal structures of UO₂SeO₃ and UO₂Se₂O₅ are known, as is the structure of UO₂(HSeO₃)₂·H₂O.[2–4] In addition, crystal structures of the rare minerals demesmaekerite, Pb₂Cu₅(SeO₃)₆(UO₂)₂(OH)₆·2H₂O, and derriksite, Cu₄(UO₂)(SeO₃)₂(OH)₆, have been described.[5,6]

The present work is a continuation to our synthetical and structural studies on metal selenites.[7–10] In the present paper we report the preparation of an ammonium uranyl selenite containing half a water of crystallisation, (NH₄)₂UO₂(SeO₃)₂·0.5H₂O, and describe its structure as well as thermal properties. We also report the structure of UO₂(HSeO₃)₂·H₂O briefly described previously, because of interesting structural similarities to the ammonium compound, and also report the thermal decomposi-

tion.[4] Comparisons are made with the structure of NH₄UO₂H(SeO₃)₂, reported in another context.[11]

## Experimental

*Preparation of the title compounds.* Crystals of (NH₄)₂UO₂(SeO₃)₂·0.5H₂O (1) were prepared by first precipitating an amorphous uranyl hydroxide by slowly adding aqueous ammonia solution to a solution of uranyl sulfate, until all uranyl was precipitated. 1.0 mol dm⁻³ solution of selenious acid was then slowly added, until the precipitate had dissolved and the pH was under 6, preferably 4–5. When the suspension was allowed to stand at 370 K for a few days, small needle-shaped crystals were obtained.

Crystals of UO₂(HSeO₃)₂·H₂O (2) could be prepared by precipitating with a solution of selenious acid from a solution of uranyl sulfate an amorphous uranyl selenite, and then slowly continuing the addition of the selenious acid until about half of the precipitate had dissolved. When the suspension was allowed to stand at 350 K for

a few days, well formed prisms of the compound were obtained.

*Thermoanalytical measurements*

Thermoanalytical measurements were carried out in a Seiko Instruments TG/DTA 320 analyzer equipped with a SSC 5200 disk station. Dynamic air and nitrogen atmospheres were used. Sample masses were 10–15 mg and the usual heating rate was 10 K min$^{-1}$. Aluminium oxide was used as reference material in DTA measurements.

*X-Ray measurements and structure solution.* A summary of the crystal data, intensity collection and refinement is given in Table 1. The unit-cell parameters for both structures were determined using 25 well centered reflections measured on a Rigaku AFC—7S diffractometer.[21] The data collections were done at 193 K with crystals fixed at the fibers using the oil-drop technique.[12]

The data were reduced by the TEXSAN program package.[13] The structure was solved using direct methods, SIR92[14] and refined by the SHELXL-93 program pack-

age.[15] The pictures were produced by the SHELXTL PLUS program package.[16]

The hydrogen atoms were found from the difference Fourier maps. The structures were refined with aniso-tropic temperature factors for the non-hydrogen atoms and isotropic factors for the hydrogen atoms. The hydro-gen atoms of the disordered ammonium ions and water of crystallization in $(NH_4)_2UO_2(SeO_3)_2 \cdot 0.5H_2O$ were not located. The temperature factor of the hydrogen atoms was fixed to be 1.5 times the $U_{eq}$ of the heavy atoms to which the hydrogens are connected. The coord-inates of non-hydrogen atoms are presented in Tables 2 and 4, and selected bond lengths and angles in Tables 3 and 5.

## Results and discussion

The structure of $(NH_4)_2UO_2(SeO_3)_2 \cdot 0.5H_2O$ is layered, as depicted in Fig. 1. The layers are formed by the two unequal selenite ions acting as bridging ligands between three and two U(VI) ions, respectively. Two selenite ions Se(1) connect four U(VI) ions, and each U(VI) is

*Table 1.* Summary crystal data, intensity collection and structure refinements for $(NH_4)_2UO_2(SeO_3)_2 \cdot 0.5H_2O$ and $UO_2(HSeO_3)_2 \cdot 2H_2O$ at 193 K.

| Empirical formula | $H_9N_2O_{8.50}Se_2U$ | $H_6O_{10}Se_2U$ |
|---|---|---|
| Formula weight | 569.04 | 543.98 |
| Diffractometer | Rigaku AFC-7S | Rigaku AFC-7S |
| Temperature/K | 193(1) | 193(1) |
| Wavelength/Å | 0.71069 | 0.71069 |
| Monochromator | Graphite crystal | Graphite crystal |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2(1)/c$ (no. 14) | $C2/c$ (no. 15) |
| Unit cell | $a=7.193(5)$ Å | $a=9.924(5)$ Å |
| | $b=10.368(5)$ Å | $b=12.546(5)$ Å |
| | $c=13.823(5)$ Å | $c=6.324(5)$ Å |
| | $\beta=91.470(5)°$ | $\beta=98.090(5)°$ |
| Volume | 1030.5(9) Å$^3$ | 779.5(8) Å$^3$ |
| $Z$ | 4 | 4 |
| $D_{calc}$ (Mg/m$^3$) | 3.668 | 4.635 |
| Absorption coeff./mm$^{-1}$ | 22.839 | 30.179 |
| Absorption corr. | Empirical, $\psi$-scan | Empirical, $\psi$-scan |
| Transmission | 1.000–0.239 | 1.000–0.763 |
| F(000) | 1004 | 944 |
| Crystal size/mm | $0.15 \times 0.12 \times 0.05$ | $0.25 \times 0.25 \times 0.2$ |
| Theta range/° | 2.83–26.50 | 2.83–26.50 |
| Index ranges | $0 \leqslant h \leqslant 9, 0 \leqslant k \leqslant 12,$ | $0 \leqslant h \leqslant 12, 0 \leqslant k \leqslant 15$ |
| | $-17 \leqslant l \leqslant 17$ | $-7 \leqslant l \leqslant 7$ |
| Scan type | $\omega$–$2\theta$ | $\omega$–$2\theta$ |
| Scan speed °/min | 3.00–15.00 | 3.00–15.00 |
| Scan range/° | 1.2 | 1.2 |
| Standard refls. | 3 every 200 | 3 every 200 |
| Reflections collected | 1963 | 809 |
| Observed reflections $(|F_o|^2 > 2\sigma|F_o|^2)$ | 1615 | 714 |
| No. of variables | 132 | 49 |
| Extinction corr. | N/A | 0.0015(3) |
| $R=\sum(||F_o|-|F_c||)/\sum|F_o|$ | 0.081 | 0.043 |
| $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]w^{1/2}$ | 0.202[a] | 0.105[b] |
| Goodnes-of-fit ($F^2$) | 1.014 | 1.057 |
| $\Delta\rho_{max/e}$ Å$^{-3}$ (near $U$) | 4.656 | 3.348 |
| $\Delta\rho_{min/e}$ Å$^{-3}$ (near $U$) | −4.433 | −3.274 |

[a]$w=1/[\sigma^2(F_o^2)+(0.128P)^2+47.14P]$. [b]$w=1/[\sigma^2(F_o^2)+(0.0689P)^2+9.14P]$, where $P=(F_o^2+2F_c^2)/3$.
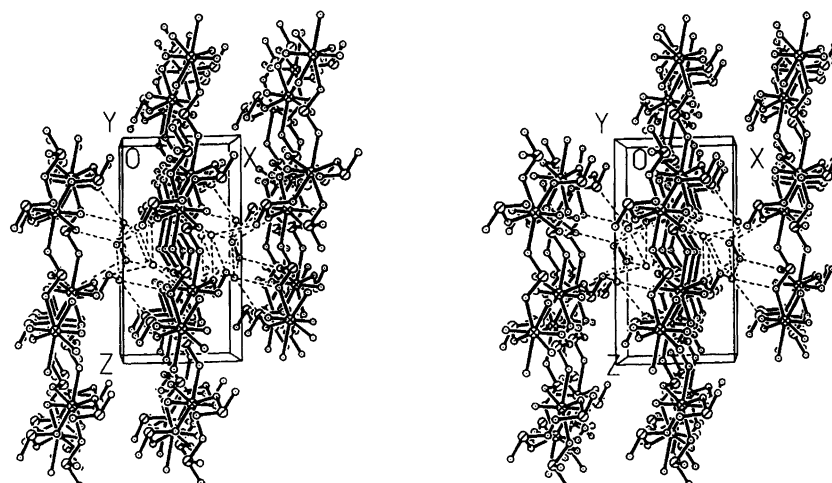
*Fig. 1.* View of the diammonium uranyl selenite hemihydrate, $(NH_4)_2UO_2(SeO_3)_2 \cdot 0.5H_2O$.

further connected by one of the Se(1) selenite ions and a Se(2) selenite ion into a fourth and fifth U(VI) ion. Thus three selenite ions Se(1) and two selenite ions Se(2) connect U(VI) ions to five others (Fig. 2). In $NH_4UO_2H(SeO_3)_2$[11] the selenite group and the hydrogen selenite group also connect a U(VI) ion to five others, as the protonated oxygen is not within bonding distance from a U(VI) ion.[11] The arrangement in the present compound is possible, since one of the Se(2) selenite ions oxygens, O(8), is not connected to a U(VI) ion. The occurence of a terminal oxygen in a selenite group, although not common, is occasionally detected. Thus $CdSeO_3 \cdot 3H_2O$ and $Al_2(SeO_3)_3 \cdot 6H_2O$ are reported to harbour such oxygens.[17,18] Two of the ammonium ions, N(1) and N(2) and the water molecule oxygen O(9), were refined with a population parameter of 0.5. The ammonium ions and the water molecule form an array, situated between the layers, which through a complex hydrogen bond network, holds the layers together (Fig. 1).

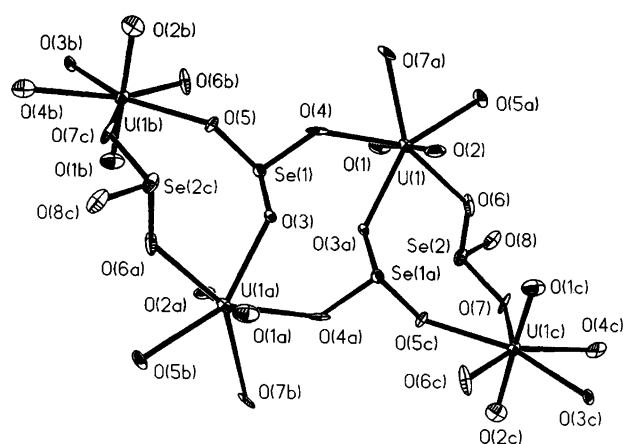The geometry of the selenite groups in



*Fig. 2.* Bridging scheme of the $(NH_4)_2UO_2(SeO_3)_2 \cdot 0.5H_2O$ along *b*. The thermal ellipsoids are drawn at the 30% probability level.

*Table 2.* Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $(NH_4)_2UO_2(SeO_3)_2 \cdot 0.5H_2O$.

| Atom | x | y | z | $U_{eq}$[a] |
|---|---|---|---|---|
| U(1) | 4361(1) | 6899(1) | −6737(1) | 18(1) |
| O(1) | 643(3) | 777(2) | −660(2) | 40(5) |
| O(2) | 235(3) | 589(2) | −688(2) | 34(5) |
| Se(1) | 5152(3) | 3640(2) | −5935(2) | 18(1) |
| O(3) | 602(2) | 521(2) | −5955(11) | 17(3) |
| O(4) | 625(3) | 299(2) | −495(2) | 33(5) |
| O(5) | 643(3) | 294(2) | −6818(13) | 27(4) |
| Se(2) | 7861(3) | 5098(3) | −8053(2) | 26(1) |
| O(6) | 571(3) | 578(2) | −7982(12) | 40(5) |
| O(7) | 749(3) | 367(2) | −8645(12) | 27(4) |
| O(8) | 881(3) | 593(2) | −8953(14) | 35(5) |
| N(1) | 974(7) | 840(4) | −869(3) | 30(11) |
| N(2) | −48(3) | 696(2) | −5297(14) | 39(12) |
| N(3) | 1257(3) | 543(2) | −9352(14) | 27(5) |
| O(9) | −38(7) | 547(4) | −543(3) | 47(12) |

[a] $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

*Table 3.* Bond lengths (in Å) and angles (in °) for $(NH_4)_2UO_2(SeO_3)_2 \cdot 0.5H_2O$.

| | | | |
|---|---|---|---|
| U(1)–O(1) | 1.74(2) | Se(1)–O(4) | 1.70(2) |
| U(1)–O(2) | 1.79(2) | Se(1)–O(5) | 1.71(2) |
| U(1)–O(6) | 2.31(2) | Se(1)–O(3) | 1.74(2) |
| U(1)–O(5)[ia] | 2.33(2) | Se(2)–O(8) | 1.67(2) |
| U(1)–O(7)[i] | 2.33(2) | Se(2)–O(7) | 1.71(2) |
| U(1)–O(3) | 2.37(2) | Se(2)–O(6) | 1.71(2) |
| U(1)–O(4)[i] | 2.38(2) | | |
| O(1)–U(1)–O(2) | 175.3(9) | O(2)–U(1)–O(7)[i] | 91.2(7) |
| O(1)–U(1)–O(6) | 88.1(9) | O(6)–U(1)–O(7)[i] | 144.7(7) |
| O(2)–U(1)–O(6) | 88.6(8) | O(5)[i]–U(1)–O(7)[i] | 72.7(6) |
| O(1)–U(1)–O(5)[i] | 92.4(9) | O(1)–U(1)–O(3) | 85.1(8) |
| O(2)–U(1)–O(5)[i] | 89.7(8) | O(2)–U(1)–O(3) | 90.9(7) |
| O(6)–U(1)–O(5)[i] | 72.0(7) | O(6)–U(1)–O(3) | 75.6(6) |
| O(1)–U(1)–O(7)[i] | 93.4(8) | O(5)[i]–U(1)–O(3) | 147.5(6) |

[a] See Table 5.

*Table 4.* Atomic coordinates ( × 10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for UO₂(HSeO₃)₂·H₂O.

| Atom | x | y | z | $U_{eq}$[a] |
|------|------|---------|--------|--------|
| U(1) | 5000 | 1935(1) | 2500 | 5(1) |
| Se(1) | 6665(1) | 3868(1) | −712(2) | 7(1) |
| O(1) | 3919(10) | 1934(7) | 5(2) | 15(2) |
| O(2) | 5000 | −27(4) | 2500 | 11(3) |
| O(3) | 6189(3) | 3470(4) | 1615(7) | 10(2) |
| O(4) | 8325(3) | 3633(4) | −339(7) | 11(2) |
| O(5) | 6677(4) | 5229(4) | −71(6) | 11(2) |

[a] $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

*Table 5.* Bond lengths (in Å) and angles (in °) for UO₂(HSeO₃)₂·H₂O.

| | | | |
|---|---|---|---|
| U(1)–O(1) | 1.755(10) | Se(1)—O(4) | 1.657(3) |
| U(1)–O(3) | 2.367(4) | Se(1)–O(3) | 1.683(4) |
| U(1)–O(4)ⁱⁱ | 2.404(2) | Se(1)-O(5) | 1.754(5) |
| U(1)–O(2) | 2.461(5) | | |
| O(1)–U(1)–O(1)ⁱ | 179.9(2) | O(1)ⁱ–U(1)–O(4)ⁱⁱⁱ | 96.6(3) |
| O(1)–U(1)–O(3) | 93.2(3) | O(4)ⁱⁱ–U(1)–O(4)ⁱⁱⁱ | 145.5(2) |
| O(1)ⁱ–U(1)–O(3) | 86.9(3) | O(1)–U(1)–O(2) | 90.0(3) |
| O(3)–U(1)–O(3)ⁱ | 71.0(2) | O(3)–U(1)–O(2) | 144.48(7) |
| O(1)–U(1)–O(4)ⁱⁱ | 96.6(3) | O(4)ⁱⁱ–U(1)–O(2) | 72.76(11) |
| O(1)ⁱ–U(1)–O(4)ⁱⁱ | 83.4(3) | O(4)–Se(1)–O(3) | 102.6(3) |
| O(3)–U(1)–O(4)ⁱⁱ | 141.57(5) | O(4)–Se(1)–O(5) | 99.6(2) |
| O(3)ⁱ–U(1)–O(4)ⁱⁱ | 72.5(2) | O(3)–Se(1)–O(5) | 94.6(2) |
| O(1)–U(1)–O(4)ⁱⁱⁱ | 83.4(3) | Se(1)–O(3)–U(1) | 131.2(3) |

Symmetry transformations used to generate equivalent atoms: ⁱ $-x+1, y, -z+1/2$; ⁱⁱ $x-1/2, -y+1/2, z+1/2$; ⁱⁱⁱ $-x+3/2, -y+1/2, -z$.

(NH₄)₂UO₂(SeO₃)₂·0.5H₂O shows Se–O bond lengths slightly longer than normally observed values of 1.65–1.69 Å .[2–4,22] The bond range is 1.70(2)–1.74(2) Å for Se(1) and 1.670(12)–1.71(2) Å for Se(2). The shortest bond length is to the uncoordinated oxygen O(8). The bond angles are 99.3(9)–102.8(8)° and 98.4(7)–104.3(10)°, respectively, which shows that both selenite groups are slightly more flat than usual. In NH₄UO₂H(SeO₃)₂ the Se–O bond range is 1.688(6)–1.700(7) Å and the bond angle range is 99.1(3)–101.2(3)° in the selenite group.[11]

In UO₂(HSeO₃)₂·0.5H₂O the hydrogen selenite group acts as a bridging ligand between two consecutive U(VI) ions, leading to a structure of one-dimensional zigzag chains (Fig. 3). These chains run approximately parallel to the *ab*-plane. The protonated oxygen of the hydrogen selenite ion is not bonded to a U(VI) ion but instead forms a contact to a selenium of an adjacent chain with a Se···O distance of 2.98(1) Å, a Se···H(5) distance of 2.25(2) and a Se–H(5)–O(5) angle of 149(1)°.

In UO₂(HSeO₃)₂·H₂O, the hydrogen selenite ion exhibits geometry frequently encountered in compounds of hydrogen selenite ions. Thus the shortest of the Se–O bond lengths, 1.657(3)Å to O(4), is of the same order as the two shortest Se–O bonds in Zn(HSeO₂)₂·2H₂O, which are 1.665 and 1.670 Å, while the other shorter Se–O distance to O(3) is 1.683(4) Å. The protonated
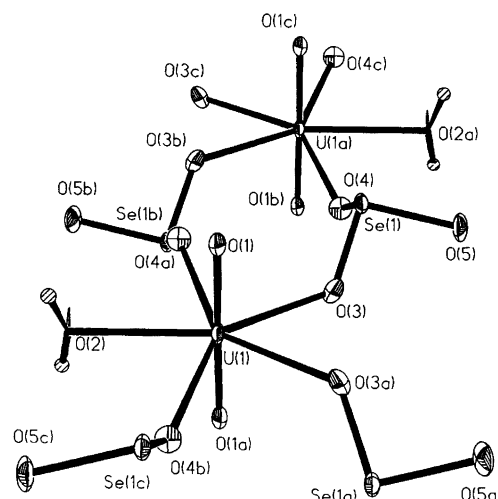


*Fig. 3.* Bridging scheme of the uranyl hydrogen selenite monohydrate, UO₂(HSeO₃)₂·H₂O. The temperature ellipsoids are drawn at 30% probability.

oxygen O(5) in the title compound is at a distance of 1.754(5) Å from the Se, as compared with 1.786 Å in the Zn compound.[19] In NH₄UO₂H(SeO₃)₂ the corresponding lengths in the hydrogen selenite ion are 1.675(7), 1.683(6) and 1.743(8) Å.[11] The protonated oxygen O(5) has a hydrogen H(5) at a distance of 0.820 Å. In Zn(HSeO₃)₂·2H₂O the O–H bond length determined with neutron diffraction is 0.967 Å.[13]

In (NH₄)₂UO₂(SeO₃)₂·0.5H₂O the coordination sphere of the U(VI) ion with seven oxygen atoms is a pentagonal bipyramid with two short and five long U–O bonds. The two oxygen atoms with short bonds lie at 1.74(2) and 1.79(2) Å from the U(VI) ion, forming a bond angle of 175.3(9)°. Three of the five oxygens lying on the pentagonal plane are contributed by three different Se(1) selenite ion oxygens, while the two remaining ones belong to two different Se(2) selenite groups. These U–O bonding distances range between 2.31(2) and 2.38(2) Å. The geometry of the coordination sphere is sligthly distorted as compared to that of UO₂(HSeO₃)₂·H₂O, in which the coordination polyhedron around the U(VI) ion is also a pentagonal bipyramid. The apex oxygen atoms are connected to the U(VI) ion with the short bonds [2 × 1.755(10) Å], while the five equatorial oxygens have a bond range 2.367(4)–2.461(5) Å.

The coordination geometries of U(VI) ions in both compounds are very similar to that in NH₄UO₂H(SeO₃)₂ with the bonds of the pentagonal bipyramid 1.77(7)–1.779(6) and 2.325(6)–2.417(6) Å, and in UO₂Se₂O₅, in which the coordination polyhedra of the two independent U(VI) are also pentagonal bipyramids with two short [1.768(8)–1.769(7) and 1.770(9)–1.770(9) Å, respectively] and five long [2.338(7)–2.480(7) and 2.326(8)–2.495(7) Å, respectively] U–O distances.[3] Another example of pentagonal bipyramid coordination in compounds of uranyl selenite ions is in Pb₂Cu₅(SeO₃)₆(UO₂)₂(OH)₆·2H₂O, where the
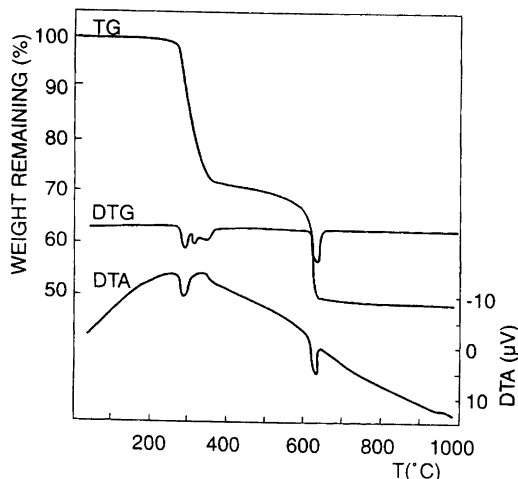
*Fig. 4.* The TG, DTG and DTA curves for $(NH_4)_2UO_2(SeO_3)_2 \cdot 0.5H_2O$ in air.



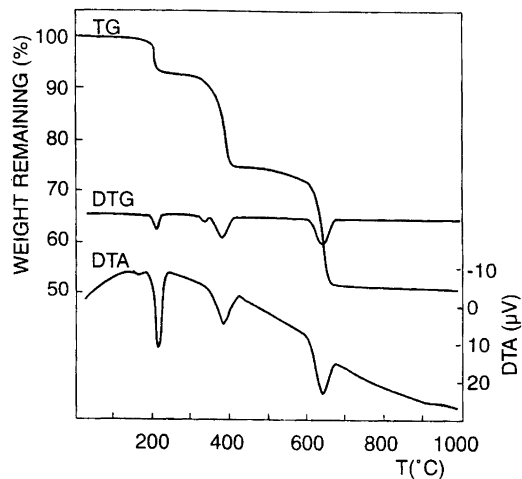*Fig. 5.* The TG, DTG and DTA curves for $UO_2(HSeO_3)_2 \cdot H_2O$ in air.

two short U–O bonds range from 1.73(2) to 1.76(2) Å and the five long ones from 2.33(2) to 2.49(1) Å.[4] In $UO_2SeO_3$ the coordination polyhedron is a more unusual hexagonal bipyramid, with 1.72(1) Å for the short bonds and 2.39(6)–2.64(1) Å for the long ones.[2] In $Cu_4(UO_2)(SeO_3)_2(OH)_6$ the uranium(VI) ion appeared with six coordination as a tetragonal bipyramid with the short U–O distances between 1.772(16) and 1.780(17) Å and the four long ones between 2.296(9) and 2.310(9) Å.[5]

The TG curves of both compounds were approximately the same in air and nitrogen atmospheres. The thermal decomposition of $(NH_4)_2UO_2(SeO_3)_2 \cdot 0.5H_2O$ in air starts at 570 K with an endothermic decomposition reaction, followed by an exothermic one (Fig. 4). The exothermic DTA peak is weak, however. Both reactions occur in a single thermogravimetric step, but the DTG curve shows the presence of two or three stages. The observed weight loss is 27.7%, which corresponds to the formation of a phase with a composition of $UO_2SeO_3$ with approximately a fifth of selenium dioxide from the other original selenite group still remaining. The plateau of the mixed phase extends from 640 to 870 K with a gradual slowly increasing weight loss; the decomposition reaches a plateau at 930 K, with an observed weight loss of 23.0%, corresponding to a formation of the oxide $U_3O_8$ (calc. 23.7%). The whole decomposition is observed to be 50.9%, while that calculated for $(NH_4)_2UO_2(SeO_3)_2 \cdot 0.5H_2O$ to $U_3O_8$ is 50.7%. The values are close enough to confirm the formula of the compound in which the water molecule has population parameter of 0.5.

The thermal decomposition compares interestingly with that of $UO_2(HSeO_3)_2 \cdot H_2O$ in air, which starts with a loss of water between 420 and 500 K (Fig. 5). The observed weight loss, 6.6%, corresponds well with the calculated weight loss (6.62%) for the loss of both the

water of crystallisation and one of the protonated oxygens in the form of water. The remaining phase of the plateau between 500 and 560 K corresponds to the formula $UO_2SeO_3 \cdot SeO_2$, or $UO_2Se_2O_5$. After this, the decomposition proceeds to another plateau between 690 and 860 K. The observed weight loss, 18.4%, corresponds approximately to loss of the $SeO_2$ in the previous phases, leading to $UO_2SeO_3$ with still some additional $SeO_2$ (approximately a fifth) remaining. The calculated weight loss to $UO_2SeO_3$ is 20.4%. The final weight loss starting at 860 K is 23.1%, and the end product is the oxide $U_3O_8$ from 950 K onwards. The total observed weight loss is 48.2% (calculated 48.4%). Thus, according to calculated values, both compounds seem to form similar phases of uranyl selenite with additional selenium dioxide, which also exhibit similar thermal decomposition mechanisms to uranium oxide. This decomposition scheme is, except for small differences in stability ranges, similar to that found for $UO_3 \cdot 2SeO_2 \cdot 2H_2O$, for which the authors postulate the obviously erroneous formula $UO_2Se_2O_5 \cdot 2H_2O$.[20]

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