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Synthesis and thermal decomposition of some selenates of gold

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Abstract

The synthesis of $HAu(SeO_4)_2$ and $MAu(SeO_4)_2$, where M is K, Rb or Cs, is described. The synthesis of $Au_2O_3 \cdot 5.2H_2O$, as a starting substance for double selenates, is presented also. The synthesized compounds were investigated by chemical and thermal analysis. The chemical compositions of the samples were confirmed and reactions of thermal decomposition were determined.

Keywords: Caesium compound; Decomposition; Gold compound; Potassium compound; Rubidium compound; Selenate; Synthesis

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1. Introduction

Very old data [1,2] for the selenates of gold are cited by Pascal [3]. Mitscherlich [1] was the first person to report on the selenates of gold, which he obtained by dissolving gold directly in selenic acid. Confirmation for the existence of gold selenates was obtained by the work of Lenher [2]; he isolated yellow crystals to which he ascribed the formula $Au_2(SeO_4)_3$. His note is very important, to the effect that this compound is not stable towards light or heat. It is necessary here to mention the recent work of Coldwell and Eddy [4] on the dissolution of gold in

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selenic acid in dependence on the concentration of selenic acid, the temperature and the time of heating. Their investigations showed that only concentrated selenic acid dissolves gold, and that dissolution requires heating for ≈ 13 days with 87% or for 13 h with 98% selenic acid at a temperature of 154°C. The yellow crystals were isolated after the addition of water to the solution obtained. Coldwell and Eddy defined the crystals as $Au_2(SeO_4)_3$. This substance has been used for imparting a violet color to glass. No other data have been presented on the synthesis of gold selenates.

In this paper, the synthesis of gold(III) hydrogenselenate and double selenates of gold(III) with potassium, rubidium and cesium is presented. The synthesis and thermal decomposition of hydrated oxide of gold(III), as the starting substance, are also discussed.

2. Experimental

Gold of purity 99.99% and selenic acid, from BDH, Poole, UK, was used for synthesis of the selenates of gold. The other chemicals were of standard quality for synthesis.

2.1. Synthesis of the compounds

2.1.1. Synthesis of hydrated gold(III) oxide

The synthesis of hydrated gold(III) oxide was performed as described in the literature [5].

The 99.99% gold was dissolved in aqua regia and the soln. was evaporated several times with HCl to remove NO_3^- ions. Distilled water was added to the dry residue and, with mixing, a solution of sodium carbonate was added to adjust the pH to 7–8. The mixture was heated at 70–80°C until evolution of CO_2 was complete. The resulting brown precipitate was collected on a G4 glass frit, washed with distilled water and dried by menas of a vacuum pump at room temperature. The material obtained was amorphous under X-ray examination.

2.1.2. Synthesis of double selenates

The freshly synthesized hydrated gold(III) oxide was dissolved in concentrated selenic acid. The dissolution was performed with gentle heating and mixing of the solution. Around 20 cm^3 of the solution so prepared and M_2SeO_4 (M is K, Rb or Cs) were put in three glass vessels; the molar ratio of Au to M was 1:3. The solutions were slowly evaporated on a hot plate until they reached very small volume (if evaporation was too rapid, crystals of selenic acid separated on the sides of the vessels). Yellow precipitates separated after the solutions had stood overnight. The precipitates were filtered off on G4 glass frits, washed several times with glacial acetic acid, and dried using a vacuum pump. The compounds obtained were stored in the dark in a vacuum desiccator containing NaOH as desiccant. Washing with water or an organic solvent, such as ethanol, methanol or ether, caused darkening and decomposition of the precipitates. Satisfactory results were obtained for compounds of potassium and rubidium. Attempts were made to synthesize gold(III) selenates with increased molar ratios of Au to M (1 : 5 and 1 : 6), but the results were not satisfactory.

2.1.3. Synthesis of gold selenates via $H[AuCl_4]$

The 99.99% gold was dissolved in aqua regia and the soln. was repeatedly evaporated with HCl until all nitrate ions had been eliminated. Distilled water was added to the residue, and the resulting solution was transferred to a 250 cm^3 volumetric flask and diluted to volume with distilled water.

To 50 cm^3 of this solution, containing 0.5 g of gold, 5 cm^3 of concentrated selenic acid and M_2SeO_4 were added to give a molar ratio of Au to M is 1 : 3 (M is K, Rb or Cs). In one vessel were placed only 50 cm^3 of the prepared $HAuCl_4$ solution and 5 cm^3 of concentrated selenic acid. The solutions were evaporated, at first on a water bath and then on a sand bath, to a minute volume. The precipitates were filtered off, washed, dried and stored exactly as for the selenates synthesized above. Satisfactory results were obtained in this way for gold(III) hydrogenselenate and cesium gold(III) selenate.

2.2. Methods and apparatus

Chemical and thermal analysis were carried out on the compounds synthesized above. The contents of gold and selenium were determined by a method worked out by us [6], involving reduction of the gold and selenium with hydrazinium ions to the elemental state under different conditions and weighing in this form.

Some thermal analyses was performed on a NETZSCH STA 429 Thermoanalyser and others on a Mettler TA-1 analyser in an atmosphere of dry air over the temperature range 20–650°C, with α-Al_2O_3 as reference substance and a platinum crucible.

The X-ray powder diffraction patterns were recorded on a Guinier-de-Wolf Camera, from Enraf-Nonius Delft, with use of Cu Kα radiation.

3. Results and discusion

The results of the chemical and thermal analyses on the most successful products of synthesis by the above procedures are given in Table 1. The calculated results are given in parentheses.

It should be pointed out that gold selenates, like gold sulfates [7], are not stable on exposure to light and moisture, and therefore all investigations were made with freshly synthesized samples. The compounds contained different amounts of acetic acid (which was used for washing the precipitates) and selenic acid, which explains why the experimental results given in Table 1 do not agree with the calculated values. The molar ratios of Au and Se given in Table 1 show that the obtained compounds have the empirical formula $MAu(SeO_4)_2$, where M is K, Rb or Cs. The

Table 1
Results of the chemical and thermal analysis of some selenates of gold

Compounds	Au/%	Se/%	molar ratio Au : Se	mass loss/%
$KAu(SeO_4)_2$	35.1	28.4	1 : 2.02	40.8
$M_r = 523.981$	(37.59)	(30.14)	(1 : 2)	(41.08)
$RbAu(SeO_4)_2$	32.1	26.6	1 : 2.07	36.6
$M_r = 570.349$	(34.53)	(27.69)	(1 : 2)	(37.73)
$CsAu(SeO_4)_2$	31.55	27.0	1 : 2.13	31.8
$M_r = 617.784$	(31.88)	(25.56)	(1 : 2)	(34.82)
$HAu(SeO_4)_2$	39.0	31.0	1 : 1.98	59.0
$M_r = 485.897$	(40.54)	(32.50)	(1 : 2)	(59.30)

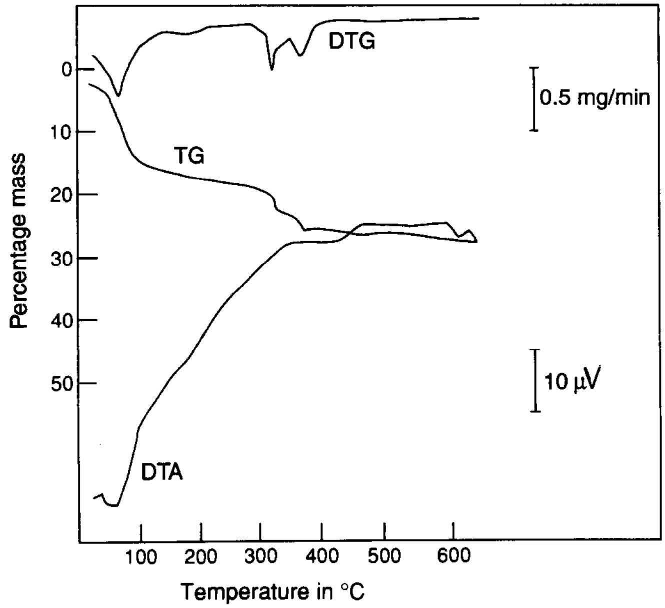

Fig. 1. TG, DTG and DTA curves of $Au_2O_3 \cdot 5.2H_2O$.

mass losses given in Table 1 correspond to the temperature range 320–650°C, where $MAu(SeO_4)_2$ were decomposing.

The TG, DTG and DTA curves of $Au_2O_3 \cdot 5.2H_2O$ in air at a heating rate of 4°C min^{-1} are given in Fig. 1. There are several steps of thermal decomposition on the TG curve. At ≈ 160°C the mass loss is 17.49%, which is in agreement with 5.2 H_2O molecules. After that, the thermal decomposition takes place in two steps.

From the foregoing, the reaction of the thermal decomposition can be presented as

$$\begin{aligned} &Au_2O_3 \cdot 5.2H_2O \xrightarrow{I} Au_2O_3 \ (<160°C) \\ &Au_2O_3 \xrightarrow{II} Au_2O \ (160\text{–}345°C) \qquad (1) \\ &Au_2O \xrightarrow{III} 2Au \ (>345°C) \end{aligned}$$

Particular phases from the thermal decomposition were not isolated. The mass loss to 650°C was 27.65%, and that calculated after reaction (1) is 26.44%. The X-ray powder diffraction patterns recorded on the residue of thermal decomposition. The *d* values (2.34, 1.43, 1.22 and 1.17 Å) showed that the residue contains only gold in the elemental state.

Fig. 2 shows the TG, DTG and DTA curves of $KAu(SeO_4)_2$, isolated after the dissolution of $Au_2O_3 \cdot 5.2H_2O$ in concentrated selenic acid. It is evident that this compound loses 6.42% of its mass up to 230°C, originating from the release of acetic acid. From 230 to 315°C the mass loss is 0.51%, in accordance with 0.02 mol of selenic acid. The decomposition of the selenate begins above 315°C and takes place in two steps. The maxima on the DTG curve are at ≈ 375°C and (the smaller one) at ≈ 410°C. The mass loss from 315 to 650°C is 40.08%, in agreement with the loss calculated (41.08%) from reaction (2).

The thermal decomposition of rubidium gold(III) selenate is presented in Fig. 3. This compound contains 5.9% of acetic acid and 1.65% of selenic acid, which were released below 320°C. The decomposition of selenate itself takes place from 320°C, again in two steps, with the DTG maximum at ≈ 375°C and a smaller peak at

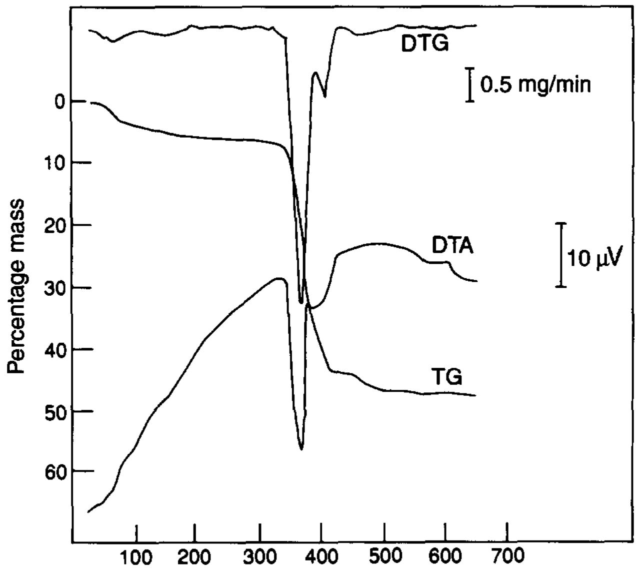

Fig. 2. TG, DTG and DTA curves of $KAu(SeO_4)_2$.

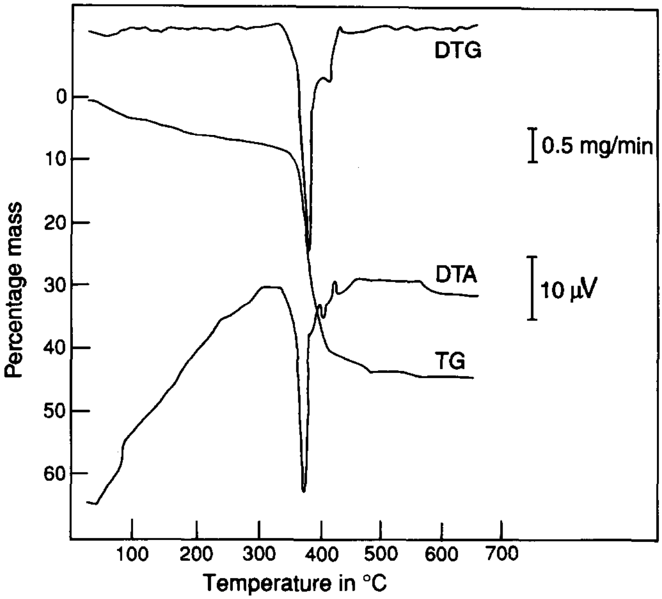

Fig. 3. TG, DTG and DTA curves of $RbAu(SeO_4)_2$.

415°C. The mass loss from 320 to 650°C is 36.8%, and that calculated from reaction (2) is 37.73%.

The TG, DTG and DSC curves for the double selenate of cesium and gold were recorded in air with a Mettler 3000 analyser at a heating rate of 2°C $\min^{-1}$. This compound (Fig. 4) contains 3.77% of acetic acid and 7.61% of selenic acid, which were released up to 300°C. The decomposition of the double selenate takes place above 320 °C. The DTG maximum is at ≈ 373°C, with a smaller peak at ≈ 408°C, and the DSC maximum is at ≈ 380°C. The loss mass from 320 to 500°C is 31.8%, compared with a calculated value of 34.82%.

From the above, the reaction of thermal decomposition for double selenates can be presented as

$$2MAu(SeO_4)_2 \xrightarrow{I} M_2SeO_4 + Au_2O_3 + 3SeO_2 + 1.5O_2$$

$$Au_2O_3 + M_2SeO_4 \xrightarrow{II} 2Au + M_2SeO_4 + 1.5O_2$$

or generally

$$2MAu(SeO_4)_2 \xrightarrow{III} 2Au + M_2SeO_4 + 3SeO_2 + 3O_2 \quad (\text{M is K, Rb, Cs}) \quad (2)$$

Fig. 5 gives the TG, DTA and differential DTA curves of the compound $HAu(SeO_4)_2$. These curves were recorded on the NETZSCH thermoanalyser. This

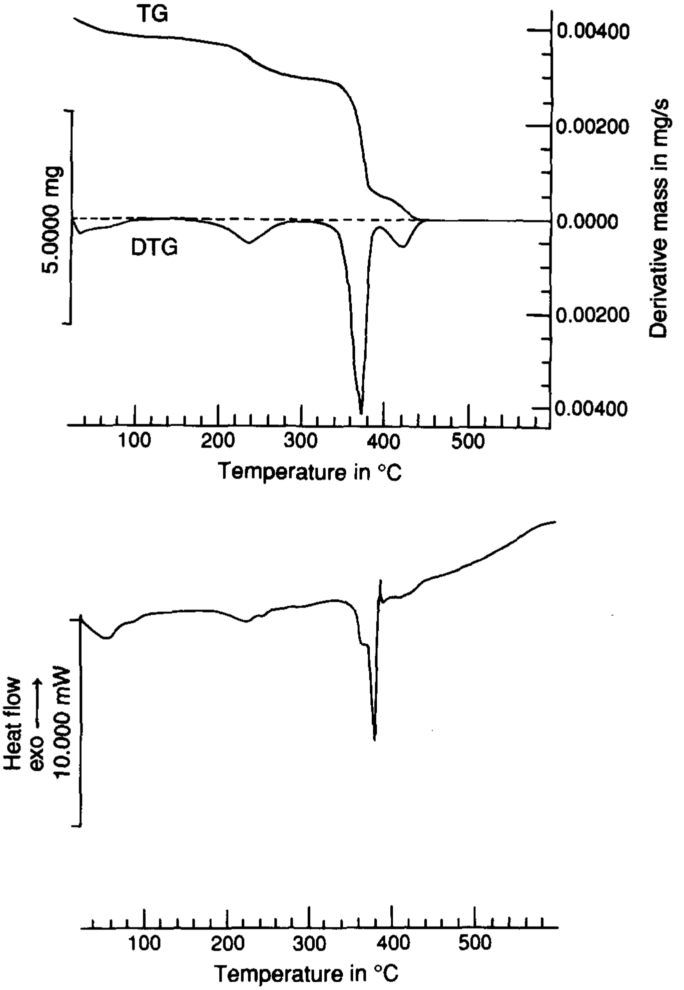

Fig. 4. TG, DTG and DSC curves of $CeAu(SeO_4)_2$.

compound contains 7.3% of acetic acid, which was released up to 185°C. The maximum of the endothermic effect which originates from the thermal decomposition of the selenate itself is at ≈408°C. The mass loss from 185 to 600°C is 59.3%, and that calculated on the basis of reaction (3) is 59.00%.

The reaction of thermal decomposition is thus

$$2HAu(SeO_4)_2 \longrightarrow 2Au + H_2O + 4SeO_2 + 3.5O_2 \qquad (3)$$

For the all compounds mentioned above, Guinier diagrams were recorded, but it was shown that the compounds are X-ray amorphous.

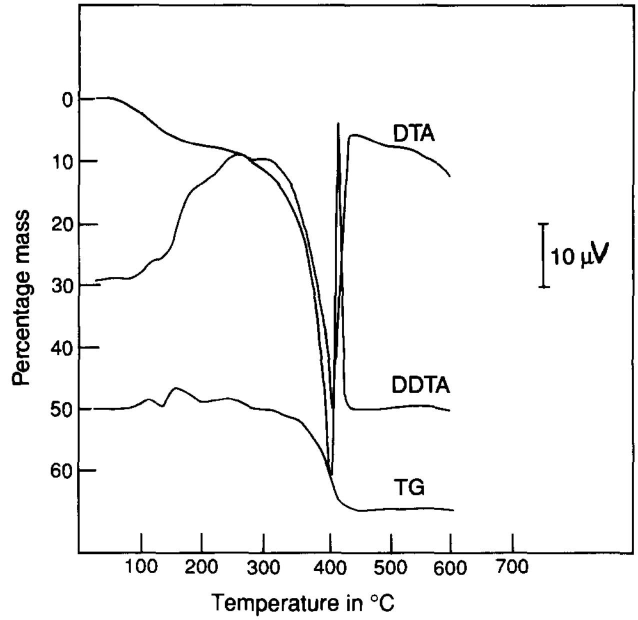

Fig. 5. TG, DTA and differential DTA curves of $HAu(SeO_4)_2$.

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