Bulletin of the Chemists and Technologists of Macedonia, Vol. 15, No. 1, pp. 23 – 28 (1996)

GHTMDD – 267
Received: December 1, 1995

ISSN 350 – 0136
UDC 546.226.07 : 543.57

Original scientific paper

SYNTHESIS AND THERMAL DECOMPOSITION OF SOME GOLD SULPHATES

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The synthesis of $AuHSO_4$ and $MAu(SO_4)_2$, where M = K, Rb or Cs, by anodic oxidation of gold in concentrated sulphuric acid is presented. The synthesized compounds were investigated by x-ray powder diffraction. The chemical composition of the compounds was confirmed, as their stability at room temperature and reactions of the thermal decomposition.

Key words: cesium compound; decomposition; gold compound; potassium compound; rubidium compound; sulphates; synthesis

INTRODUCTION

There is limited data about sulphates of gold. Some data [1–5] about solubility of the gold in the concentrated sulphuric acid in presence of different oxidizing agents are already presented. It has been pointed out that the obtained solutions were hydrolyzed very fast and also that the oxidation state of gold in these solution is unknown.

Jirsa and Buryanek [6], studied the solubility of the fresh precipitated gold(III) hydroxide in the concentrated sulphuric acid, as well as, the anodic oxidation of gold. They obtained solution in which gold is in form of $Au_2(SO_4)_3$. One year later Jirsa and Jelinek [7, 8] reported that in the sulphuric acid solution the gold is present in the form of $H[Au(SO_4)_2]$ but it is rapidly dissociated to Au^{3+} ions. Prat [9] has described $Au_2(SO_4)_3$, as red powder substance.

By the reaction of concentrated sulphuric acid and auril nitrate, Schotlander [10] isolated a yellow powder substance which is mixed with a small quantity of gold. He formulated it as a auryl hydrogen sulphate. His investigations indicated that it is very hygroscopic. In presence of water it is rapidly decomposed to gold(III) hydroxide and sulphuric acid. In reaction of potassium hydrogen sulphate and auryl hydrogen sulphate, by heating to 200 °C, the same author got yellow crystals with empirical formula $Au_2(SO_4)_3 \cdot K_2SO_4$. He also obtained yellow crystals, in reaction of silver sulphate and auryl hydrogen sulphate. According to Schotlander [10] these compounds are more stable then the auryl hydrogen sulphate. At low temperature the compounds hydrolyse slowly and at high temperature rapidly by releasing sulphuric acid.

Up until now, there is no any other data about sulphates of gold but we have prepared some selenates of gold [11] as a part of our research program on gold compounds. The aim of the present work is synthesis and thermal decomposition of gold(I) hydrogen sulphate and double sulphates of gold(III) with potassium, rubidium and cesium.

EXPERIMENTAL

The gold used for synthesis of golden sulphates was of 99.99% purity. The other chemicals were with standard quality for synthesis.

Procedure

For the synthesis of the compounds firstly a solution of gold(III) sulphate by anodic oxidation of gold in concentrated sulphuric acid [6, 7, 8] was prepared.

A cathode and anode of gold were immersed in 120 cm^3 concentrated sulphuric acid. The cathode was separated from anode with a diaphragm mode of porcelain, from the firm Holdenwanger, Berlin. The electrolysis was performed at voltage of 4V and 100 mA electric current. After 60 hours a quantity of 6.95 g of gold was dissolved (faster electrolysis, effects releasion of gold in elemental state).

In each of vessels 20 cm^3 were put of the prepared solution of the sulphate of gold. The potassium, rubidium or cesium sulphate, were added in the three of them in such a quantity in order to obtain molar ratio M : Au = 1 : 1 (M = K, Rb or Cs). These three solutions were evaporated on a hot plate to very small volumes and the fourth solution, in which there was no alkaline sulphate, was evaporated to dryness. The precipitates were filtrated through glass frit G4, washed with acetic acid glacialicum and dried in vacuum, using NaOH. The obtained precipitates of double gold(III) sulphates were yellow-orange color, instead of gold(I) hydrogen sulphate, which is dark-red color.

These compounds are very sensitive to light, moisture and organic solvents, such as ethyl alcohol, methyl alcohol and ether. Since they were rapidly decomposed, it was necessary to analyze them immediately.

Apparatus and methods

The gold was determined using gravimetric method [12] by reducing it into metal. The reduction was performed with hidrazinium in quantity to reach pH = 10.5 – 11. The sulphates were determined gravimetrically as $BaSO_4$.

The thermoanalytical investigations were performed on Mettler-TA 1 thermoanalyser in dry air atmosphere with heating rate 4 °C/min, in the range 25–500 °C using platinium crucibles, and α-Al_2O_3 as reference substance.

The x-ray powder diffraction patterns of the prepared samples and also of the residues of the thermal decomposition were obtained on Guinier-de Wolf camera by the firm Enraf-Nonius Delf, with Cu-K_α radiation.

RESULTS AND DISCUSSION

The results of the quantitative determination of gold and sulphates are given in Table I. As can be seen, there is some disagreement between the theoretical and the experimental values. This is due to the sensitivity of the compounds obtained, to light, moisture, organic solvents etc. The compounds are amorphous and they easily adsorb impurities. Thus, it was proved that each compound contains adsorbed acetic acid (which was used for washing) and sulphuric acid too. The compounds with general formula $MAu(SO_4)_2$ contain, $MHSO_4$ and Au_2O_3 as well. The presence of acetic acid and particularity of sulphuric acid, was confirmed by the investigation into thermal decomposition. On the other hand, the presence of $MHSO_4$ was confirmed by the x-ray powder diffraction patterns. Namely, the obtained compounds are amorphous, so on the obtained diffractograms, there are peaks generally of $MHSO_4$ (Table III). There were no peaks of metallic gold, but according to the results of the chemical analysis, it could be considered that the compounds contain amorphous Au_2O_3 as an impurity.

The TG, DTG and DTA curves of $AuHSO_4$ are given on Fig. 1. The compound contains 2.41% adhered acetic acid, which is removed at about 190 °C. There are no weight loss changes in the temperature range from 190 to 295 °C. After that the thermal decomposition of $AuHSO_4$ takes place in one stage. It is realized in the temperature range from 295 to 420 °C with maximum on DTG curve at about 390 °C. The weight loss up to 500 °C is 31.03% and calculated weight loss according to the reaction

$$2AuHSO_4 \longrightarrow 2Au + 2SO_3 + H_2O + \frac{1}{2}O_2$$

is 33.00 %. That is for about 2.00 % higher than experimental obtained. This can be explain, probably, by the presence of little amounts of elemental gold in the compound. (See Table I)

Table I

The results of the chemical analysis of the compounds

Compounds	Au %	SO_4^{2-} %	Molar ratio Au : SO_4^{2-}
$AuHSO_4$ Mr = 294.035	68.30 (66.99)	32.00 (33.01)	1 : 1.04 (1 : 1)
$KAu(SO_4)_2$ Mr = 428.192	44.80 (45.80)	43.00 (45.12)	1 : 1.97 (1 : 2)
$RbAu(SO_4)_2$ Mr = 476.557	36.80 (41.33)	36.90 (40.73)	1 : 1.96 (1 : 2)
$CsAu(SO_4)_2$ Mr = 523.992	36.10 (37.59)	31.60 (37.04)	1 : 1.80 (1 : 2)

*Calculated values are given in parenthesis.

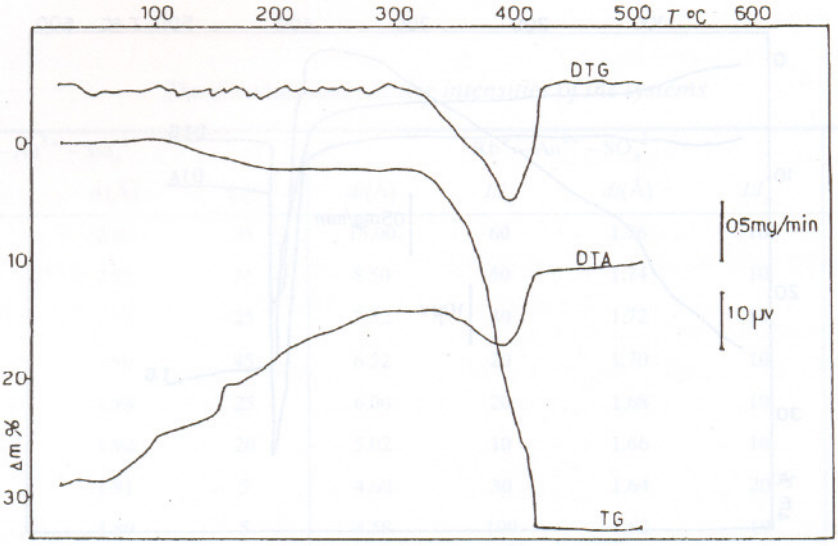

Fig. 1. TG, DTG and DTA curves of $AuHSO_4$

In Table II the results of x-ray powder diffraction patterns of $AuHSO_4$ are given.

Table II

The d-values and relative intensities of $AuHSO_4$

$d/(Å)$	I/I_o	$d/(Å)$	I/I_o	$d/(Å)$	I/I_o	$d/(Å)$	I/I_o
7.00	80	2.44	10	1.64	10	1.26	5
5.38	100	2.38	10	1.60	10	1.25	10
5.02	80	2.30	30	1.58	5	1.23	10
4.38	60	2.10	50	1.56	5	1.22	10
3.90	90	2.03	30	1.55	5		
3.75	100	1.88	10	1.52	5		
3.60	30	1.86	20	1.49	5		
3.50	20	1.83	10	1.48	10		
3.48	10	1.82	10	1.46	5		
2.95	30	1.81	10	1.43	10		
2.88	60	1.78	10	1.39	5		
2.65	30	1,76	10	1.36	10		
2.58	40	1.72	10	1.34	5		
2.52	70	1.67	20	1.27	5		

The diagrams of thermal decomposition of double sulphates are given in Fig.'s 2–4. The diagrams of these compounds could be interpreted, taking into consideration that they contain acetic and sulphuric acid as was mentioned above. In accordance with TG curves, the compounds of potassium contains 3.48 % acetic and sulphuric acid, the compound of rubidium 9.02 % and compound of cesium 5.69 % respectively. In all compounds releasion of acetic and sulphuric acid takes place at 230 °C. After that, the compounds begin to decompose. The maximum on DTG curves is at about 415 °C for each compound. In general the reaction of thermal decomposition can be expressed as:

$$2MAu(SO_4)_2 \longrightarrow 2Au + 3SO_3 + \frac{3}{2}O_2 + M_2SO_4$$

(M = K, Rb, or Cs)

The weight loss from 230–505 °C of the potassium compound is 23.76 % (33.65 %), of the rubidium compound 21.78 % (30.35 %) and of the cesium compound is 18.14 % (27.60 %) respectively. It is less than the calculated one for each compound. For the compound of potassium it is about 9.89 %, at compound of rubidium is for 8.57 % and at compound of cesium is for 9.46 %. As mentioned above, this is due to the presence of $MHSO_4$ and gold(III) oxide hydrate in the compounds.

The small maximum on DTA curves in Fig. 3–4 at 430 °C to about 440 °C can be explained with the probable transformation of $MHSO_4$ to M_2SO_4, where M=Rb or Cs [13]. This transformation is not registred on the DTG curves completly separated with endothermic maximum, since it may be overlapped by the big DTG endothermic maximum from the thermal decomposition of $MAu(SO_4)_2$. The thermal decomposition of the present gold(III) oxyd takes place at the same temperature range [11] as these compounds. The residue of the thermal decomposition (elemental gold and M_2SO_4) was confirmed by the x-ray powder diffraction patterns.

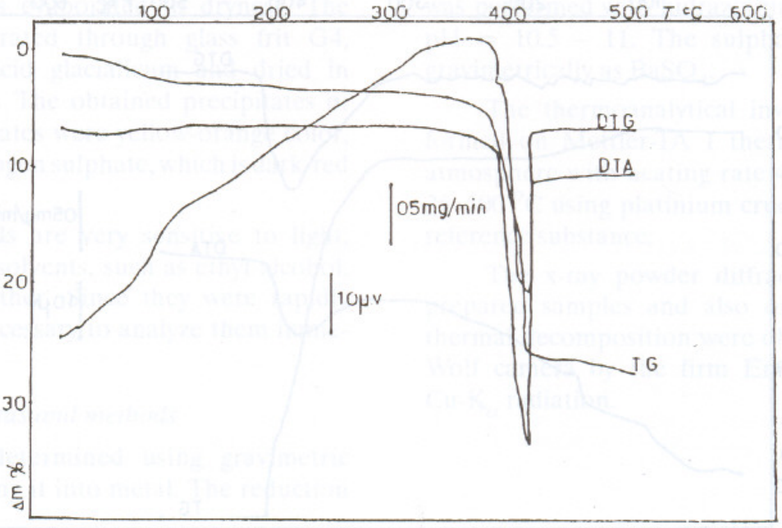

Fig. 2. TG, DTG and DTA curves of $KAu(SO_4)_2$

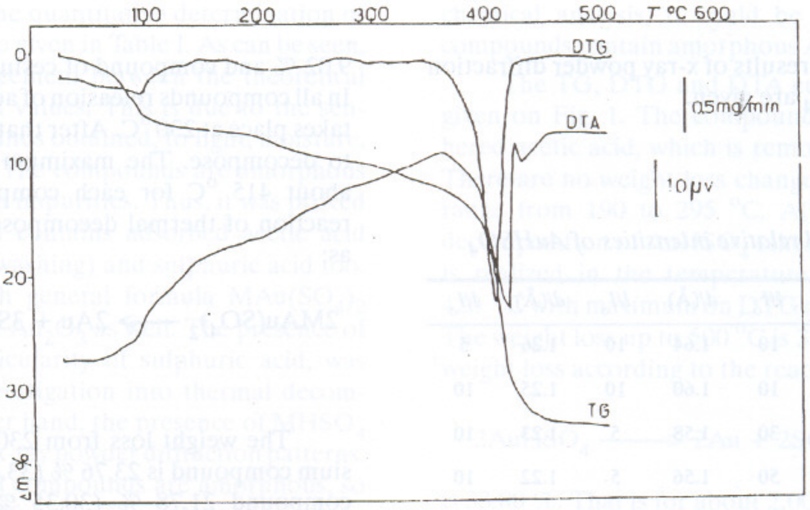

Fig. 3. TG, DTG and DTA curves of $RbAu(SO_4)_2$

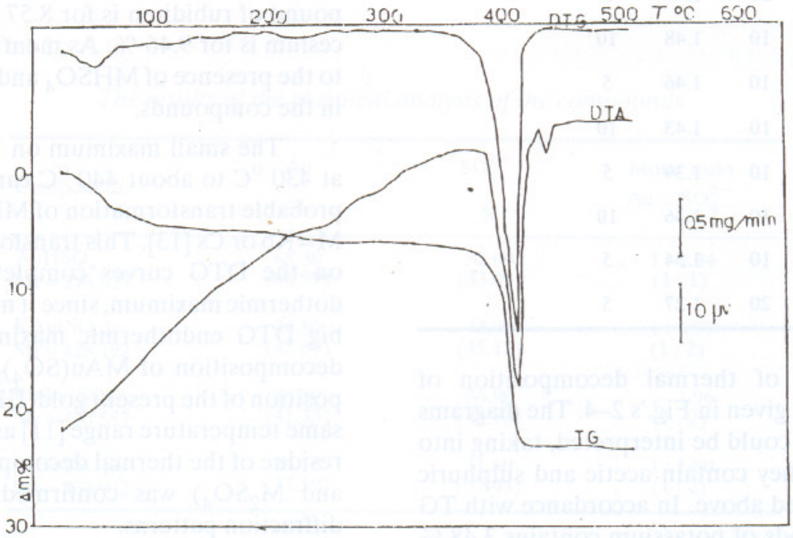

Fig. 4. TG, DTG and DTA curves of $CsAu(SO_4)_2$

Table III

The d-values and relative intensities of the systems

$K^+ - Au^{3+} - SO_4^{2-}$				$Rb^+ - Au^{3+} - SO_4^{2-}$				$Cs+ - Au^{3+} - SO_4^{2-}$	
d/(Å)	I/I_o	d/(Å)	I/I_o	d/(Å)	I/I_o	d/(Å)	I/I_o	d/(Å)	I/I_o
5.80	90	2.02	35	15.00	60	1.76	10	9.00	5
4.85	50	2.01	35	8.50	50	1.74	10	4.65	5
4.75	5	1.97	25	7.52	30	1.72	10	4.40	5
4.47	5	1.96	45	6.52	20	1.70	10	4.10	5
4.33	45	1.93	25	6.00	20	1.68	10	3.82	100
4.12	55	1.92	20	5.02	10	1.66	10	3.50	10
3.92	45	1.91	5	4.60	30	1.64	20	3.10	10
3.84	50	1.89	5	4.58	100	1.62	10	2.92	10
3.60	60	1.88	5	4.30	30	1.60	20	2.80	5
3.50	40	1.87	20	4.02	30			2.75	5
3.39	40	1.84	20	3.85	20			2.35	5
3.24	35	1.83	5	3.70	100			2.25	5
3.12	100	1.80	15	3.48	50			2.20	5
3.00	25	1.78	45	3.28	40			2.15	5
2.98	100	1.73	25	3.15	50				
2.95	5	1.66	10	3.05	30				
2.88	35	1.65	10	3.00	50				
2.81	10	1.63	10	2.86	40				
2.76	25	1.61	25	2.66	50				
2.73	45	1.57	10	2.60	60				
2.71	35	1.55	25	2.45	20				
2.66	10	1.52	15	2.40	30				
2.59	25	1.49	25	2.35	30				
2.57	15	1.48	20	2.30	20				
2.47	3	1.47	40	2.25	30				
2.42	20	1.44	10	2.24	10				
2.40	15	1.43	10	2.22	10				
2.36	10	1.42	20	2.18	10				
2.33	70	1.40	10	2.13	10				
2.32	10	1.37	5	2.10	20				
2.26	10	1.36	5	2.04	20				
2.25	5	1.34	5	2.01	20				
2.19	20	1.32	15	2.87	20				
2.17	20	1.31	5	2.86	10				
2.15	10	1.30	10	2.84	10				
2.13	25	1.29	10	2.83	10				
2.11	55	1.27	20	2.80	20				
2.06	30			2.78	20				

CONCLUSIONS

From the discussion given above it can be concluded that:

1. $AuHSO_4$ and $MAu(SO_4)_2$ where M = K, Rb or Cs were synthesized by anodic oxidation of gold in concentrated sulphuric acid.

2. The synthesized compounds always contained a certain percent of acetic acid, sulphuric acid, $MHSO_4$ and Au_2O_3.

3. These compounds are very sensitive to light, moisture and organic solvents, such as ethyl alcohol, methyl alcohol and ether. Since they decomposed rapidly it was necessary to analyze them immediately.

4. The thermal investigation and x-ray diffraction showed that $AuHSO_4$ decomposed to elemental gold and $MAu(SO_4)_2$ to elemental gold and M_2SO_4.

5. After the removal of acetic acid at 190 °C the decomposition of $AuHSO_4$ takes place in one stage in the temperature range from 295 to 420 °C.

6. The thermal decomposition of $MAu(SO_4)_2$ is similar; after removal of acetic acid and sulphuric acid to 230 °C, it decomposes from 230 to about 450 °C.

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Резиме

СИНТЕЗА И ТЕРМИЧКО РАСПАЃАЊЕ НА НЕКОИ СУЛФАТИ НА ЗЛАТОТО

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Клучни зборови: соединенија на цезиумот; термичко распаѓање; соединенија на златото; соединенија на калиумот; соединенија на рубидиумот; сулфати; синтези

Направена е синтеза на $AuHSO_4$ и $MAu(SO_4)_2$ каде што M=K, Rb или Cs. Златото беше растворано со анодна оксидација на елементарно злато во концентрирана сулфурна киселина. Синтетизираните соединенија се испитувани со рендгенска анализа на прашкасти примероци. Хемискиот состав е потврден и со хемиска анализа на добиените соединенија. Определена е стабилноста на соединенијата на собна температура, како и реакциите на термичкото распаѓање со помош на TG, DTG и DTA мерења.