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Investigation of thermal properties of double complex salts $[M(NH_3)_5Br][AuBr_4]_2{\cdot}nH_2O$, M = Rh, Ir

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Abstract Novel double complex salts $[M(NH_3)_5Br][AuBr_4]_2{\cdot}nH_2O$, M = Rh, Ir, have been synthesized and examined. The processes of thermal decomposition of the compounds in inert and reductive atmospheres have been studied and intermediate products identified. Simultaneous thermal analysis with parallel mass-spectrometric analysis of evolved gases (STA-EGA) has been employed for identification of main gaseous products of thermolysis in inert atmosphere. It has been revealed that the final products of decomposition in inert or reductive atmospheres are fine powders of gold and the corresponding platinum metal with sizes of crystallites 4–40 nm. The possibility of preparation of the metastable solid solution $Au_{0.05}Ir_{0.95}$ on thermolysis of $[Ir(NH_3)_5Br][AuBr_4]_2{\cdot}H_2O$ in inert atmosphere has been demonstrated.

Keywords Double complex salts · TG · DTA · STA · Thermal decomposition · Platinum metal complexes · Gold complexes

Introduction

Gold-containing metallic systems on oxide supports exhibit high-catalytic activity in low-temperature oxidation of CO [1]. Introduction of minor amount of platinum metals essentially enhances stability of ultrafine gold particles and extends the operating time of a catalyst [2]. Double complex salts containing a complex cation of one metal and a complex anion of another one are promising precursors for production of ultrafine polymetallic systems. Thermal decomposition of such compounds occurring at moderate temperatures allows tailoring of polymetallic systems possessing predefined properties. The composition of such systems can be strictly defined already at the stage of double complex salt preparation [3, 4]. Earlier, we have obtained a series of double complex salts of general formula $[M(NH_3)_5Cl][AuCl_4]Cl{\cdot}nH_2O$, M = Ir, Rh, Ru, Cr, $n = 0$–1 [5, 6]. Crystal structures of the compounds have been determined and thermal properties studied. It has been demonstrated that metastable phases of solid solutions with rather large content of the components can be obtained for the systems of metals unmixable even in liquid state (Ir–Au and Rh–Au) at comparatively low temperatures (<400 °C). It is noteworthy that preparation of such materials by other techniques seems hardly possible.

The purpose of this study was the synthesis and examination of double complex salts involving $[M(NH_3)_5Br]^{2+}$ cations and $[AuBr_4]^-$ anions. The major focus is made on investigation of the thermal behavior of the compounds obtained in different atmospheres, identification of the intermediate products of thermolysis, and examination of metallic powders—the final products of thermal decomposition.

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Experimental

Starting compounds $[Ir(NH_3)_5Br]Br_2$ and $[Rh(NH_3)_5Br]Br_2$ were prepared as described in the literature [7]. The solution of $H[AuBr_4]$ was prepared by dissolution of gold (99.99%) in a mixture of concentrated HNO_3 and HBr followed by concentration with addition of aqueous HBr.

Synthesis of $[M(NH_3)_5Br][AuBr_4]_2 \cdot nH_2O$

175 mL of 0.01 M solution of $[M(NH_3)_5Br]Br_2$ warmed to 60–80 °C was combined with 9.1 mL of 0.382 M solution of $H[AuBr_4]$ under stirring. The ratio M:Au in the reaction mixture was 1:2. On cooling to room temperature, the solution afforded shiny brown crystals. The reaction mixture was cooled to 5 °C in order to enhance the yield. The precipitated crystals were collected by filtration, rinsed with cold water, and dried in air. Yields varied within 60–70%.

Powder X-ray diffraction studies were carried out on a diffractometer DRON-SEIFERT-RM4 (Cu K_α radiation, graphite monochromator at the diffracted beam, scintillation detector with amplitude discrimination).

The products of thermolysis were indexed using the data for pure metals and compounds given in the PDF database [8]. Parameters of the phases were refined using least-squares technique applied to all data with PowderCell program [9]. The sizes of crystallites (d) in the prepared bimetallic particles were determined using integral broadening of isolated diffraction peaks with WINFIT 1.2.1 program [10].

The sum of metals was determined by reduction of a sample placed in a molten quartz boat by passing a hydrogen stream at 400 °C [11].

Found for $[M(NH_3)_5Br][AuBr_4]_2 \cdot nH_2O$/calculated for $[M(NH_3)_5Br][AuBr_4]_2 \cdot H_2O$,%: Rh + Au 37.0 ± 0.4/37.7; Ir + Au 41.3 ± 0.5/41.6.

Thermogravimetric experiments in hydrogen atmosphere were carried out on a Q-1000 derivatograph modified for operation in different atmospheres. Simultaneous thermal analysis was made on an STA 409 PC Luxx® device (NETZSCH) coupled with a gas analyzer QMS 100 Series. Open Al_2O_3 crucibles were used, loads ~20 mg, heating rate 10 K/min, helium stream 60 mL/min.

Results and discussion

TGA studies performed has revealed that the first stage of decomposition of both double complex salts in air, helium, or hydrogen atmosphere is an irreversible lost of crystallization water within temperature range 130–180 °C, which, in contrast to chloride complex salts $[M(NH_3)_5Cl][AuCl_4]Cl \cdot nH_2O$, is clearly manifested at the TG curve. Upon that the original compounds are converted to new double complex salt of different structure and do not absorb any measurable amount of water when stored in air for a long time afterwards.

Further decomposition of the $[Ir(NH_3)_5Br][AuBr_4]_2 \cdot nH_2O$ in inert atmosphere (Fig. 1) is similar to the decomposition of $[Ir(NH_3)_5Cl][AuCl_4]Cl \cdot nH_2O$ (Fig. 2). The second decomposition stage occurs within temperature range 220–320 °C and is accompanied by an endo effect, the major gaseous product being Br_2 (Fig. 1). According to powder diffraction data, the intermediate product obtained at 320 °C is a mixture of metallic gold (d = 20–30 nm) and $[Ir(NH_3)_5Br]Br_2$. Thermal processes occurring within temperature range 340–520 °C correspond to decomposition of $[Ir(NH_3)_5Br]Br_2$. The compound decomposes in two stages, both are accompanied by endo effects. Corresponding main gaseous products are NH_3, N_2, and Br_2 (Fig. 1). The final product of thermolysis at 700 °C is a mixture of metallic gold (d = 8–12 nm) and a solid solution of composition $Au_{0.05}Ir_{0.95}$ (d = 7–10 nm). The data obtained are summarized in Eq. 1 of decomposition of $[Ir(NH_3)_5Br][AuBr_4]_2 \cdot nH_2O$ in inert atmosphere:

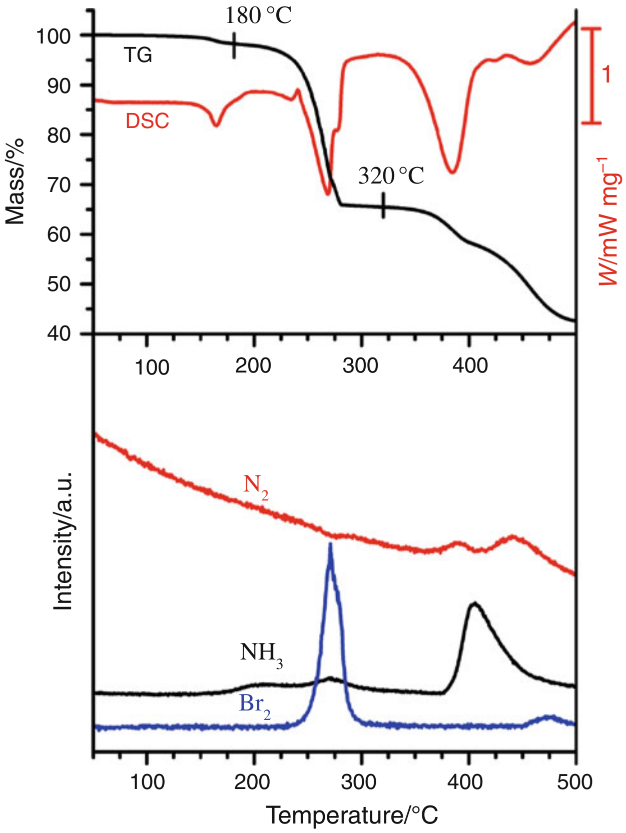

Fig. 1 TG, DSC, and MS for $[Ir(NH_3)_5Br][AuBr_4]_2 \cdot nH_2O$ in He atmosphere at heating rate 10 K min^{-1}

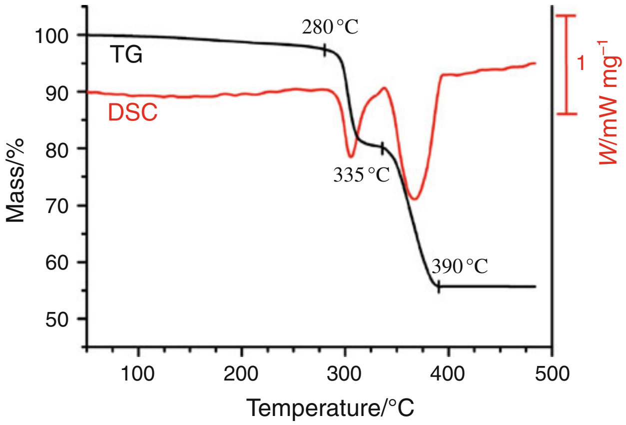

Fig. 2 TG and DSC curves of $[Ir(NH_3)_5Cl][AuCl_4]Cl\cdot nH_2O$ in He atmosphere at heating rate 10 K min^{-1}

$$[Ir(NH_3)_5Br][AuBr_4]_2\cdot nH_2O \xrightarrow[-H_2O]{130-180\,^\circ C} [Ir(NH_3)_5Br][AuBr_4]_2 \xrightarrow[-Br_2]{200-300\,^\circ C} Au + [Ir(NH_3)_5Br]Br_2 \xrightarrow[-Br_2-NH_3-N_2]{350-500\,^\circ C} Au + Ir \qquad (1)$$

When the process is carried out in hydrogen atmosphere, the temperature of the beginning of decomposition of the anionic part of the double complex salt and the final decomposition temperature are reduced (Fig. 3). At the temperature of 320 °C, the intermediate product again is a two-phase mixture of Au and $[Ir(NH_3)_5Br]Br_2$. The final product at temperature 400 °C is a two-phase mixture of fine powders of gold ($d = 23$–33 nm) and iridium ($d = 4$–8 nm).

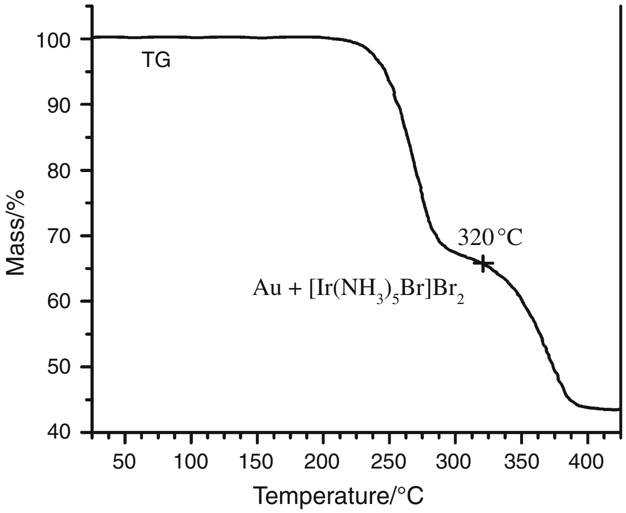

Fig. 3 TG curve for $[Ir(NH_3)_5Br][AuBr_4]_2$ in H_2 atmosphere at heating rate 10 K min^{-1}

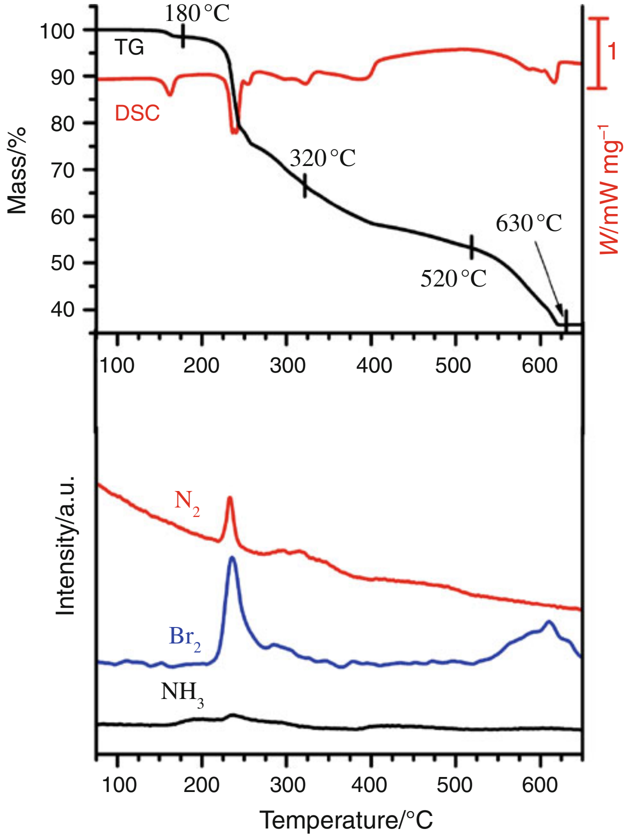

Fig. 4 TG, DSC, and MS for $[Rh(NH_3)_5Br][AuBr_4]_2\cdot nH_2O$ in He atmosphere at heating rate 10 K min^{-1}

After the loss of the crystallization water, decomposition of $[Rh(NH_3)_5Br][AuBr_4]_2\cdot nH_2O$ (Fig. 4) in inert atmosphere occurs in a more complex manner than that of $[Rh(NH_3)_5Cl][AuCl_4]Cl\cdot nH_2O$ (Fig. 5). A weight loss is observed within temperature range 180–270 °C, which is accompanied by an endo effect. Mass-spectrometry data evidence that, in addition to bromine, dinitrogen is evolved (Fig. 4), thus indicating simultaneous decomposition of the anionic and cationic parts of the double complex salt. When thermolysis was terminated at 320 °C, powder XRD revealed the presence of metallic gold, $[Rh(NH_3)_5Br]Br_2$, and a phase of unknown composition (X), which was not identified with this technique. Further heating to 520 °C results in formation of a mixture Au ($d = 35$–45 nm) + $RhBr_3$, as confirmed by powder XRD. The final stage of thermolysis occurring within 520–630 °C is decomposition of $RhBr_3$ with development of the phase of metallic rhodium and evolution of gaseous Br_2 (Fig. 4). The final product of thermolysis of $[Rh(NH_3)_5Br][AuBr_4]_2\cdot nH_2O$ in inert atmosphere at 700 °C is a two-phase mixture of powders of metallic gold ($d = 20$–26 nm) and rhodium ($d = 23$–35 nm). It should be noted that the course of the decomposition process within temperature range 270–630 °C is similar to decomposition of pure $[Rh(NH_3)_5Br]Br_2$, which is stable in inert atmosphere up to the temperatures of approximately 280 °C [12]. The above provides grounds to

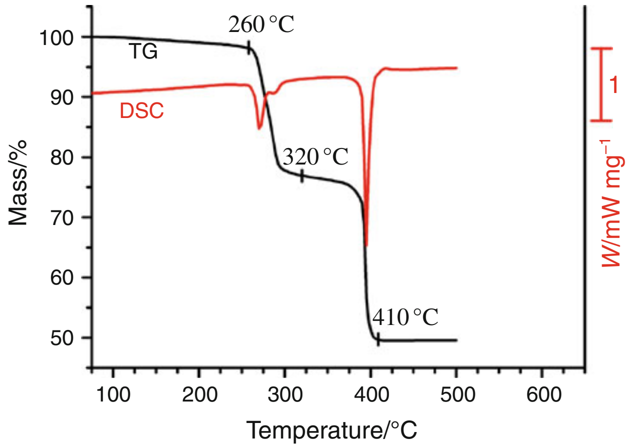

Fig. 5 TG and DSC curves of $[Rh(NH_3)_5Cl][AuCl_4]Cl{\cdot}nH_2O$ in He atmosphere at heating rate 10 K min^{-1}

suppose that the unknown phase (X) is the ammine rhodium complex $[Rh(NH_3)_3Br_3]$. The processes of thermal decomposition of $[Rh(NH_3)_5Br][AuBr_4]_2{\cdot}nH_2O$ in inert atmosphere can be described by Eq. 2:

$$\begin{aligned}
&[Rh(NH_3)_5Br][AuBr_4]_2 \cdot nH_2O \xrightarrow[-H_2O]{130-180\,^{\circ}C} \\
&\quad [Rh(NH_3)_5Br][AuBr_4]_2 \xrightarrow[-(Br_2+N_2+NH_3)]{200-320\,^{\circ}C} \\
&\quad Au + \left[Rh(NH_3)_5Br\right]Br_2 \xrightarrow[-(NH_3+N_2)]{320-520\,^{\circ}C} RhBr_3 \\
&\quad + Au \xrightarrow[-(Br_2)]{520-625\,^{\circ}C} Rh + Au \qquad (2)
\end{aligned}$$

Decomposition of $[Rh(NH_3)_5Br][AuBr_4]_2{\cdot}nH_2O$ in hydrogen atmosphere (Fig. 6) is completed at the temperature of 400 °C. Up to the temperature of ~300 °C, the course of the decomposition almost entirely follows the decomposition in inert atmosphere, however, further a rapid weight loss occurs, and the TG curve does not have horizontal sections related to formation of stable intermediates. The difference lays in the absence of formation of $RhBr_3$ during thermolysis, as confirmed by powder XRD of the intermediate product obtained at the temperature of 320 °C. The final product at 420 °C is a two-phase mixture of fine powders of gold (d = 25–40 nm) and rhodium (d = 9–13 nm).

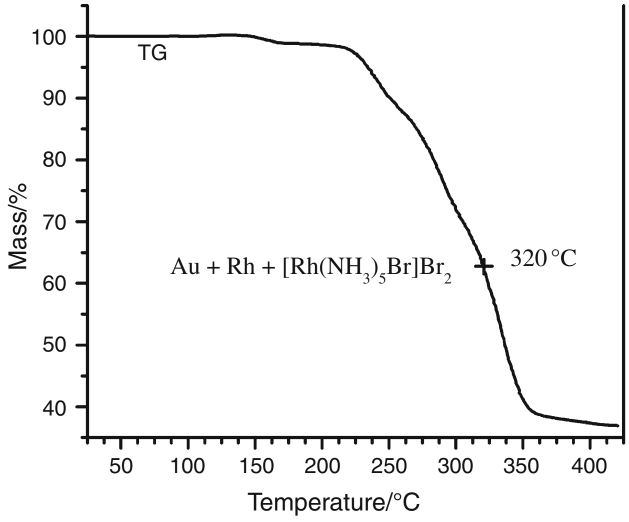

Fig. 6 TG curve for $[Rh(NH_3)_5Br][AuBr_4]_2{\cdot}nH_2O$ in H_2 atmosphere at heating rate 10 K min^{-1}

The initial temperature of decomposition of complexes containing anions $[AuBr_4]^-$, as a rule, smaller than that of complexes containing anions $[AuCl_4]^-$ that is in good consistency with that Br^- is better reductant than Cl^-. The smaller thermal stability for substances containing Br^- according to Cl^- is fully consistent with literature data. Therefore, for example, under the same conditions of thermolysis the initial temperature of decomposition for $K[AuCl_4]$ is 145 °C, but for $Rb[AuBr_4]$ is 125 °C [13]. In case of double complex salts $[Co(NH_3)_6][AuX_4]X_2$ (where X = Cl, Br), the initial temperature of decomposition for $[Co(NH_3)_6][AuCl_4]Cl_2$ is 210 °C, but for $[Co(NH_3)_6][AuBr_4]Br_2$ only 185 °C [14].

Conclusions

The processes of thermal decomposition of $[Ir(NH_3)_5Br][AuBr_4]_2{\cdot}nH_2O$ and $[Rh(NH_3)_5Br][AuBr_4]_2{\cdot}nH_2O$ in inert and reductive atmospheres have been studied. It has been revealed that the final products of decomposition are, as a rule, fine powders of gold and the corresponding platinum metal. The possibility of preparation of the solid solution $Au_{0.05}Ir_{0.95}$ on thermolysis of $[Ir(NH_3)_5Br][AuBr_4]_2{\cdot}H_2O$ in inert atmosphere has been demonstrated.

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