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STUDIES ON DEHYDRATION AND THERMAL DECOMPOSITION OF TRIS(2,2'-BIPYRIDYL) RUTHENIUM(II) CHLORIDE AND SULPHATE

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Tris(bipyridyl) ruthenium(II) chloride and sulphate have been synthesized and investigated using thermal analysis. It follows from the experimental data that both compounds are heptahydrates stable at room temperature.

The $[Ru(bipy)_3]^{2+}$ complex is stable up to 300°, irrespective of the nature of the anion bound with it. The final decomposition product of the chloride is metallic ruthenium, while that of the sulphate is ruthenium dioxide.

Many research centres have recently been dealing with the direct conversion of solar energy into electricity [1], and with the methods of utilization of solar radiation for water photolysis [2, 3]. Photocatalysts in systems decomposing water under the influence of solar radiation include bipyridyl-ruthenium(II) complexes [4–6]. Hydrogen liberated in this process may be utilized as an excellent fuel or as a raw material for chemical syntheses.

The present work had the aim of the synthesis of crystalline hydrates of tris(bipyridyl) ruthenium(II) chloride and sulphate, which are employed in studies on the production of hydrogen in the process of water photolysis.

Tris(bipyridyl) ruthenium(II) chloride was synthesized [7] from hydrated ruthenium(III, IV) chlorides and oxychlorides and bipyridyl in boiling dimethylformamide medium. The compound obtained was purified by crystallization from water. Tris(bipyridyl) ruthenium(II) sulphate was obtained [5] by passing an aqueous solution of $[Ru(bipy)_3]Cl_2$ through a column packed with Dowex 1 X 4 anion-exchanger, 100–200 mesh, in sulphate form. After elution of the compound from the column, water was evaporated from the solution and the separated complex was crystallized from a water–ethanol mixture.

It follows from the literature data that all attempts so far to determine the contents of crystallization water in $[Ru(bipy)_3]Cl_2$ and $[Ru(bipy)_3]SO_4$ have failed. Unambiguous conditions for its removal have not been given either. Data concerning the stabilities of these complexes and their decomposition products have not been encountered in the literature dealing with this subject. It was reported that $[Ru(bipy)_3]Cl_2$ may exist as a hexahydrate [5, 8, 9] or a pentahydrate [10, 11], undergoing decomposition at 150° [12] or at 200° in vacuo [8]. On the other hand, Braddock [7] does not mention crystallization in the $[Ru(bipy)_3]Cl_2$ complex he synthesized.

Tris(bipyridyl) ruthenium(II) sulphate synthesized by Schilt [13] and dried over magnesium perchlorate contains two molecules of crystallization water, which is lost in the course of further drying over $Mg(ClO_4)_2$ at 196°. However, Kirch [5] does not report the content of crystallization water in $[Ru(bipy)_3]SO_4$ obtained using his own method, describing its formula as $[Ru(bipy)_3]SO_4 \cdot x\ H_2O$.

Experimental

Due to the lack of unambiguous data concerning the crystallization water content, the dehydration conditions and the stability, the complexes we obtained were studied by thermal analysis, a Hungarian derivatograph being used.

Platinum crucibles, a sample weight of 200 mg, sensitivities of TG 50 mg, DTG 1/5 and DTA 1/10, and a heating rate of 2 degree/min in air were used for the determination of crystallization water content and dehydration conditions. The investigations of the stabilities of the complexes and the thermal decompositions of the salts were carried out in corundum crucibles in air atmosphere, using weighed amounts of 200 mg, a heating rate of 10 degree/min and sensitivities of TG 200 mg, DTG 1/10 and DTA 1/10. The thermal curves of the hydrated $[Ru(bipy)_3]Cl_2$ complex are shown in Fig. 1.

Results

It follows from analysis of the TG and DTG curves that the complex chloride forms a heptahydrate stable under dry air conditions. On heating, it undergoes dehydration in two distinctly marked steps: 50–100° (3 water molecules) and 120–180° (4 water molecules). The dehydration is indicated by two sharp, symmetrical DTG peaks, with maxima at 70 and 150°. They are accompanied by similar endothermic DTA peaks. The anhydrous complex chloride is stable up to 300°, exhibiting no thermal effects. Thermal decomposition of $[Ru(bipy)_3]Cl_2$ begins above 300° and proceeds in two steps, with the maximum of the DTG peak at 360° associated with an endothermic effect (DTA). Rapid decomposition, combined with a strong exothermic DTA effect associated with combustion of the sample, begins at 440°. Combustion of the organic products of decomposition proceeds to 650° and is accompanied by weight loss (TG curve) and respective DTG and exothermic (DTA) effects. The decomposition product is metallic ruthenium, which undergoes slight oxidation in air atmosphere (weight gain in TG curve).

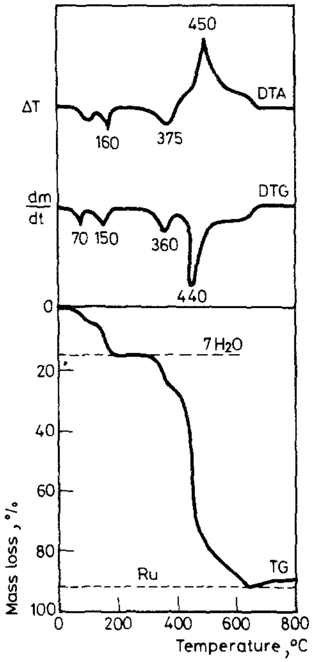

Fig. 1 TG, DTG and DTA curves of $[Ru(bipy)_3]Cl_2 \cdot 7\ H_2O$

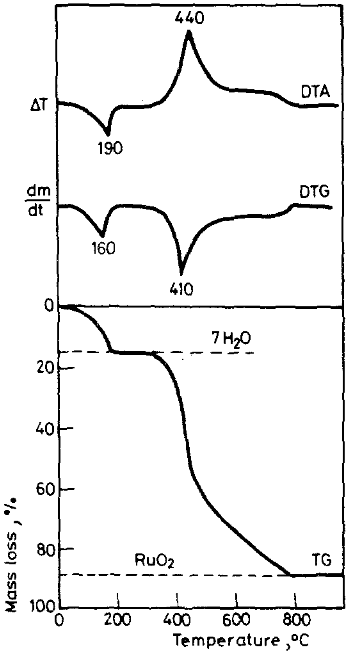

Fig. 2 TG, DTG and DTA curves of $[Ru(bipy)_3]SO_4 \cdot 7\ H_2O$

Thermal curves of hydrated $[Ru(bipy)_3]SO_4$ are shown in Fig. 2. It is a heptahydrate stable in air. On heating, it releases seven molecules of crystallization water in one step from 60 to 180°, which is recorded as a broad asymmetric DTG peak with maximum at 160°. It is accompanied by a similar asymmetric DTA peak. The anhydrous complex sulphate is stable up to 300°, not exhibiting any thermal effects. Thermal decomposition associated with an increasing exothermic effect (DTA curve) occurs above 300°. The maximum of the asymmetric DTG peak corresponding to the evolution of volatile substances is observed at 410°. The maximum of the exothermic DTA effect due to the ignition of organic decomposition products lies at 440°. The slow combustion of solid decomposition products, accompanied by continuous weight loss in the TG curve and observed as a small continuous exothermic DTA effect and a respective DTG effect, occurs at temperatures above 500°. Under the experimental conditions used, the thermal decomposition ends at 800°. The product of thermal decomposition of the $[Ru(bipy)_3]SO_4$ complex in air atmosphere is RuO_2.

As a result of thermal analysis it can be concluded that the $[Ru(bipy)_3]^{2+}$ complex is stable up to 300°, irrespective of whether the chloride or sulphate anion is bonded with it.

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Zusammenfassung — Tris(bipyridyl) ruthenium(II)-chlorid und -sulfat wurden synthetisiert und thermoanalytisch untersucht. Beide Verbindungen sind Heptahydrate und stabil bei Raumtemperatur. Der $[Ru(byp)_3]^{2+}$-Komplex ist stabil bis 300 °C, unabhängig von der Art des Anions. Endprodukt der Zersetzung des Chlorids ist metallisches Ruthenium, der des Sulfats dagegen Rutheniumdioxid.

Резюме — Проведено термическое исследование синтезированных три (бипиридил) рутений хлоридного и сульфатного комплекса. Экспериментальные результаты показали, что оба комплекса являются гептагидратами, стабильными при комнатной температуре. Катион Ru(бипиридил)$_3^{2+}$, независимо от природы аниона, является стабильным до 300°. Конечным продуктом разложения хлоридного комплекса является металлический рутений, а сульфатного — двуокись рутения.