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SYNTHESIS AND THERMAL DECOMPOSITION OF COMPLEXES OF COMPOSITION $/Ru/bpy/_3X_2$ $/X=OH^-,Cl^-,Br^-,I^-,ClO_4^-,IO_4^-,ReO_4^-$ and $VO_3^-/$

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ABSTRACT

Simple methods of synthesis of tris/bipyridine/ruthenium/II/ chloride and hydroxide have been developed from which the compounds mentioned in the title have been obtained. Spectrophotometric, X-ray and thermal investigations proved that the kind of anion has no effect no the position and shape of the absorption band in the visible region, but it influences the decomposition temperature of the complex $/Ru/bpy/_3/^{2+}$ cation, the number of decomposition steps and composition of intermediate and final products.

INTRODUCTION

The most interesting and intensively developing area of modern chemistry of ruthenium are the investigations concerning complexes of ruthenium/II/ with 2,2'-bipyridine and 1,10-phenanthroline and their derivatives /1,2/. Current interest in compounds containing the $Ru/bpy/_3/^{2+}$ complex cations stems from their luminescence, photosensitization of electron and energy transfer processes and from their photocatalytic role in solar energy conversion /3-6/.

So far, tris /2,2'-bipyridine/ruthenium/II/ chloride has been synthesized by fusion /7/ of hydrated ruthenium/III/ chloride with 2,2'-bipyridine /260°C/ or by heating of the abovementioned reactants in dimethylformamide /8/, by reduction of hydrated ruthenium /III/ chloride with hydrogen /9/ under increased pressure or by reduction with hypophosphorous acid /10/ of $RuCl_3.xH_2O$ or $K_2/RuCl_5/H_2O/$ in the presence of bipyridine.

On the other hand, tris/bipyridine/ruthenium/II/ hydroxide has been obtained by shaking aqueous suspension of silver/I/ oxide with aqueous solutions of tris/bipyridine/ruthenium/II/ chloride, bromide or iodide.

Although complexes of ruthenium/II/ with bipyridine containing Br^-, I^- and ClO_4^- anions have been known for a long time, no data concerning thermal investigations of these compounds except $/Ru/bpy/_3/Cl_2.$[illegible]H_2O and $/Ru/bpy/_3/SO_4.7H_2O$ /11/ have been found in literature.

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The purpose of our investigations was to develop a simple method of synthesis of tris/bipyridine/ruthenium/II/ chloride and hydroxide-reactants for the preparation of complexes mentioned in the title, which were subjected to thermal analysis.

EXPERIMENTAL

A new, simple method of synthesis of $/Ru/bpy/_3/Cl_2.7H_2O$ was developed, which is based on the reduction of mixture of hydrated Ru/III,IV/ chlorides with glucose and ascorbic acid in water in the presence of 2,2'-bipyridine. The obtained complex underwent ion exchange by passing its aqueous solution through a column packed with a basic anion exchanger Dowex 1x4 /100-200 mesh/ resulting in tris /bipyridine/ruthenium/II/ hydroxide containing small amount of carbonates. The complexes named in the title obtained from the compounds mentioned above as a result of reaction with appropriate acids or salts in aqueous medium were in the from of sparingly soluble precipitates, which were filtered and dried in air at ambient temperature. Visible absorption spectra of synthesized compounds /except those containing IO_4^- and OH^-/, in which ruthenium was determined thermogravimetrically and spectrophotometrically and the remaining elements - gravimetrically, were obtained using a SPECOL 10 spectrophotometer.

Thermal analysis of the discussed complexes was carried out by means of a MOM F.Paulik, J.Paulik, L.Erday derivatograph using the following parameters: sample size 100 or 200 mg /20 mg for explosive substances/, heating rate 10K/min, sensitivity: DTA - 1/10, DTG - 1/10, TG - 20, 100 or 200 mg; alundum crucibles, reference - Al_2O_3, atmosphere - air, final temperature 900°C.

The final products of thermal decomposition remaining in a crucible were subjected to X-ray phase analysis by means of a DRON-2 diffractometer using filtered CuK_α radiation and the following parameters: supply voltage 40 kV, anodic current 30 mA, goniometer speed 2°/min.

RESULTS AND DISCUSSION

Thermal and chemical analysis of the investigated compounds indicated that anhydrous complexes are: tris/bipyridine/ruthenium /II/ perchlorate, periodate and perrhenate. In contrast with the remaining compounds periodate and perchlorate are characterized by explosive combustion at temperatures 210 and 295°C, respectively. This phenomenon is probably associated with strong oxidizing properties of IO_4^- and ClO_4^- anions.

Tris /bipyridine/ruthenium/II/ bromide formsquinquehydrate. Upon heating, it loses crystallization water in one step beginning from 80-200°C with the maximum of the DTG peak at 160°C. Anhydrous compound is stable up to 310°C. Above this temperature it decomposes thermally in two steps with the corresponding DTG maxima at 360°C - with small exothermic effect - and at 480°C - with large exothermic effect associated with the combustion of organic substances. The final decomposition product of $/Ru/bpy/_3/Br_2.5H_2O$ is RuO_2.

Tris/bipyridine/ruthenium/II/ iodide forms a hydrate of the formula $/Ru/bpy/_3/I_2.4,5H_2O$. It loses crystallization water on heating in one step from 80-160°C with the maximum of the DTG peak at 140°C. Anhydrous salt is stable up to 330°C; it decomposes in two steps with slight DTA exothermic effect at 370°C and large exothermic effect with the DTA maximum at ca.400°C. The final decomposition product is also RuO_2.

Hydrated tris/bipyridine/ruthenium/II/ metavanadate, $/Ru/bpy/_3/ /VO_3/_2.5,5H_2O$, can be dehydrated above 80°C. Anhydrous compound is stable up to 350°C. It decomposes at 440°C with large DTA exothermic effect due to combustion of organic components. A DTA exothermic effect at 770°C was recorded in the final decomposition stage. It corresponded to the maximum of the DTG peak at 760°C, resulting from oxidation of the intermediate products of decomposition. As a result of these reactions, an unidentified crystalline substance of the mass corresponding to the sum $RuO_2+V_2O_5$, resulting from stoichiometry of a weighed sample used, is formed. X-ray phase analysis showed that the final product of decomposition of $/Ru/bpy/_3/VO_3/_2.5.5H_2O$ does not contain RuO_2; it consist of a new phase and an admixture of V_2O_5.

$/Ru/bpy/_3//ReO_4/_2$ is stable up to 420°C. It decomposes in 3 steps. Combustion of volatile organic substances occurs in the 420-540°C temperature range. The reaction of oxidation of carbon originating from pyrolysis proceeds at 540-720°C at the expense of reduction of ruthenium and rhenium to elemental state. Oxidation of metals combined with sublimation of Re_2O_7 occurs above 720°C in air atmosphere. The residue contains RuO_2 with a minimal admixture of rhenium. In addition to the determination of ruthenium on the basis of data from thermograms, the metal was additionally determined in elemental form, which was obtained by reduction of ruthenium /IV/ oxide with hydrogen.

CONCLUSION

It follows from the analysis of the investigated complexes that they exhibit in the visible range a characteristic absorption band at λ_{max} = 450-452 nm, corresponding to back donation /MLCT/ and similar shape of this band independent of the kind of anion.

Thermal stability of synthesized complexes /initial decomposition temperature ranging from 210 to 420°C/, the course of decomposition processes and the composition of intermediate and final products depend on the kind anions, which stabilize to a larger or smaller extent the complex $/Ru/bpy/_3/^{2+}$ cation.

It seems that one of the intermediate products of decomposition of $/Ru/bpy/_3//ReO_4/_2$ is an alloy of the composition $RuRe_2$, which was confirmed by decomposition of this compound under reduced pressure. An unexplained question remains the composition of the final product of decomposition of $/Ru/bpy/_3//VO_3/_2 \cdot 5.5H_2O$ in the form of crystalline oxide phase, contaminated by V_2O_5. Due to catalytic properties of V_2O_5 and RuO_2 it is possible that this new compound can also have an application as a catalyst.

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