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# SYNTHESIS AND THERMAL INVESTIGATIONS OF RUTHENIUM(II) PHENANTHROLINE COMPLEXES OF $[Ru(phen)_3]X_2$ TYPE, WHERE X ≡ $Cl^-$, $Br^-$, $I^-$, $SCN^-$, $VO_3^-$, $ReO_4^-$

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## ABSTRACT

A new method of synthesis of hydrated tris(phenanthroline)ruthenium(II) chloride has been developed. This chloride constitutes a reactant for preparation of the complexes listed in the title. The quantitative composition of these complexes has been established on the basis of chemical analysis and electron spectra in the metal to ligand charge transfer band region. The thermal stability of these compounds in air was examined. It was established on the basis of X-ray analysis that $RuO_2$ was the final decomposition product except for $[Ru(phen)_3](VO_3)_2$ (phen ≡ 1,10-phenanthroline), which decomposed to form a phase containing ruthenium(IV) and vanadium(V) oxides.

## INTRODUCTION

The significance of polypyridyl ruthenium(II) complexes, to which compounds containing the $[Ru(phen)_3]^{2+}$ cation also belong, results from the application of these compounds in investigations on solar energy conversion during the photolysis of water [1–4]. Consequently, recent papers on the compounds mentioned above deal mainly with the results of photochemical, photocatalytic, electrochemical, photoelectrochemical and other similar investigations, as well as the processes of electron and energy transfer.

The chemical literature contains few papers on the outer sphere interaction between anionic counterions and $[Ru(L\text{–}L)_3]^{2+}$ type complex cations, and provides no information whatever on thermal investigations of compounds containing tris(1,10-phenanthroline)ruthenium(II) cations [5]. On the other hand, phenanthroline and, particularly, dipyridyl complexes of certain transition metals, of $[M(L\text{–}L)_3]X_n$ composition [where M ≡ $Fe^{II}$, $Ni^{II}$, $Co^{II}$, $Co^{III}$, $Ru^{II}$ or $Rh^{III}$; X ≡ $Cl^-$, $Br^-$, $I^-$, $ClO_4^-$ or $\frac{1}{2}SO_4^{2-}$; L–L ≡ 1,10-phenanthroline (phen) or 2,2′-dipyridyl (2,2′-bipyridine, bpy) ] have been subjected to thermal analysis, which in some cases revealed the formation,

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within certain temperature ranges, of other compounds as intermediates in the thermal decomposition [6–20].

Our investigations were aimed at the development of a simple method of synthesis of $[Ru(phen)_3]Cl_2$, a major reactant for preparation of the compounds cited in the title, and also at the examination of the thermal stability of the obtained compounds in air.

## EXPERIMENTAL

### *Materials*

A mixture of hydrated ruthenium(III,IV) chlorides was prepared [3] from $RuO_2$, which was fused with NaOH and $Na_2O_2$. The obtained ruthenates were oxidized by sodium periodate to $RuO_4$, and the resulting $Ru^{VIII}$ oxide was reduced by hydrochloric acid to $Ru^{III,IV}$ chlorides. All the reagents used were of analytical reagent grade.

### *Preparation and chemical analysis of $[Ru(phen)_3]X_2$ type complexes*

Hydrated tris(phenanthroline)ruthenium(II) chloride was obtained [21,22] by heating, in a beaker, an aqueous alcohol mixture (80 $cm^3$ of $H_2O$ and 40 $cm^3$ of EtOH) containing 1.7 g of glucose, 4.5 g of hydrated ruthenium(III,IV) chloride (42.6% Ru content) and 11.5 g of phenanthroline hydrate, until the colour of the mixture became green. On cooling, 0.9 g of ascorbic acid dissolved in 10 $cm^3$ of $H_2O$ was added, and the mixture was reheated until the colour changed to red–orange and the volume was reduced to ca. 70 $cm^3$. Following filtration of the mixture and repeated concentration (to ca. 40 $cm^3$), the precipitate was filtered off and recrystallized from $H_2O$.

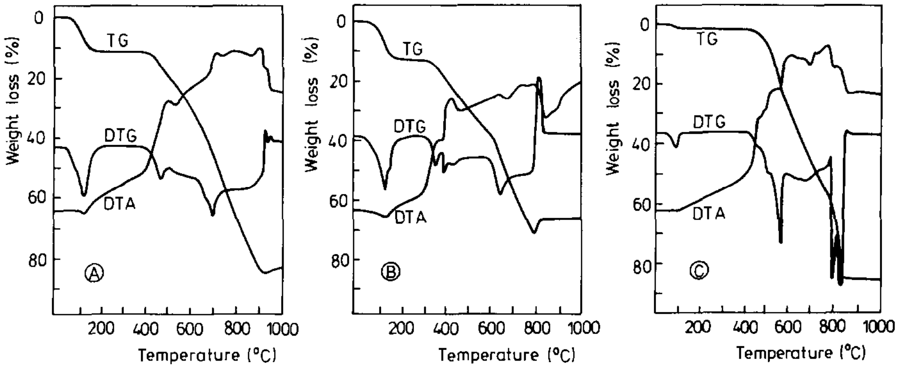

Fig. 1. Thermograms for (A) $[Ru(phen)_3]Br_2 \cdot 6.5H_2O$; (B) $[Ru(phen)_3](VO_3)_2 \cdot 7H_2O$; and (C) $[Ru(phen)_3](ReO_4)_2 \cdot H_2O$.

TABLE 1

Results of chemical analyses

| No. | Complex | Ru (%) | | M (Re, V) (%) | | X (%) [a] | | C (%) | | H (%) | | N (%) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Found. | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found | Calc. |
| **1** | $[Ru(phen)_3]Cl_2 \cdot 8H_2O$ | 11.73 | 11.80 | – | – | 8.38 | 8.28 | 50.27 | 50.47 | 4.17 | 4.66 | 8.75 | 8.81 |
| **2** | $[Ru(phen)_3]Br_2 \cdot 6.5H_2O$ | 11.14 | 11.00 | – | – | 17.39 | 17.40 | 47.27 | 47.03 | 3.88 | 4.02 | 10.70 | 9.14 |
| **3** | $[Ru(phen)_3]I_2 \cdot 3H_2O$ | 10.75 | 10.64 | – | – | 26.23 | 26.73 | 45.33 | 45.54 | 3.17 | 3.15 | 10.37 | 8.85 |
| **4** | $[Ru(phen)_3](ReO_4)_2 \cdot H_2O$ | 8.75 | 8.71 | 32.25 | 32.09 | – | – | 36.82 | 37.23 | 2.11 | 2.24 | 6.98 | 7.24 |
| **5** | $[Ru(phen)_3](VO_3)_2 \cdot 7H_2O$ | 10.45 | 10.47 | 10.10 | 10.55 | – | – | 44.74 | 44.74 | 3.75 | 3.93 | 8.63 | 8.69 |
| **6** | $[Ru(phen)_3](SCN)_2 \cdot 3H_2O$ | 12.45 | 12.67 | – | – | 14.28 | 14.31 | 55.90 | 56.17 | 3.59 | 3.69 | 14.15 | 13.79 |

[a] X ≡ halogen or $SCN^-$

The remaining complexes were obtained from $[Ru(phen)_3]Cl_2$ and the respective salts by crystallization from $H_2O$. All the preparations were dried in air at room temperature.

Halides and $SCN^-$ were determined gravimetrically in the form of AgX, ruthenium was determined spectrophotometrically [23], and rhenium and vanadium were determined thermogravimetrically (see Fig. 1). The results of chemical analysis are listed in Table 1.

### *Instruments*

Thermal analysis was carried out using a Q-1500D derivatograph (MOM) and alundum crucibles; $Al_2O_3$ served as the reference material. Atmosphere, static air; sample weight, 100 mg; heating rate, 10 K $min^{-1}$; final temperature, 1000 °C.

The final products of thermal decomposition remaining in the crucibles were analysed by X-ray diffractometry using a DRON-2 diffractometer and Cu $K\alpha$ radiation.

Absorption spectra were recorded and ruthenium was determined using a SPECOL-10 spectrophotometer.

The C, H, N analyses were performed on a Carlo Erba model 1106 elemental analyser.

## RESULTS AND DISCUSSION

Methods of synthesis of $[Ru(phen)_3]Cl_2 \cdot xH_2O$ known thus far [24–27] require application of ruthenium compounds of composition $K_2[Ru(OH)Cl_5]$ [24] or $K_2[Ru(H_2O)Cl_5]$ [26], reduced with freshly prepared $NaH_2PO_2$ in the presence of phenanthroline. Phosphate ions formed in these reactions contaminate the $[Ru(phen)_3]Cl_2$ and are hard to remove, as has been thoroughly examined in the synthesis of $[Ru(bpy)_3]Cl_2$ [28]. On the other hand, preparation of tris(phenanthroline)ruthenium(II) chloride from hydrated ruthenium(III,IV) chloride in dimethylformamide [25] is cumbersome because of the complicated isolation of the synthesized product from the reaction mixture, and syntheses carried out in ethanol [27] require a long reaction time (72 h).

Consequently, a more convenient method of synthesis of $[Ru(phen)_3]Cl_2$, based on two-stage reduction of ruthenium with glucose and, subsequently, ascorbic acid, has been developed.

Apart from its reductive properties, glucose in a $Ru^{III,IV}$–phenanthroline–water–ethanol system catalyses the complexation of ruthenium by phenanthroline, which results in formation of green $[Ru(phen)_3]^{3+}$ ions in the solution. Complexed ruthenium is reduced by a stronger reducing agent, i.e. ascorbic acid, not to the free metal, but to $[Ru(phen)_3]^{2+}$ cations, which crystallize in the form of an orange hydrated chloride.

The remaining compounds were obtained by a double exchange reaction

$$[Ru(phen)_3]Cl_2 + 2MX = [Ru(phen)_3]X_2 + 2MCl \quad (1)$$

which took advantage of the lower solubility of these compounds compared with $[Ru(phen)_3]Cl_2$.

All the discussed complexes are slightly hydroscopic in air, and their solubility decreases with an increase in the radius of the anionic counterion.

Electron spectra of these compounds in the metal to ligand charge transfer region ($\lambda_{max} = 448$ nm) had a shape similar to the spectrum of tris(phenanthroline)ruthenium(II) chloride, and were consistent with the literature data [29–31]; this enabled the application of spectrophotometry for the quantitative determination of ruthenium.

The results of thermal investigations are presented in Table 2, and examples of thermograms are illustrated in Fig. 1.

It has been established during the investigations that, in all the studied cases, loss of water of crystallization on heating is a continuous process, and is accompanied by an endothermic effect. Initial temperatures of thermal decomposition of the anhydrous complexes vary between 330 and 430 °C and depend, similarly to solubility, on the outer sphere effect of the anionic counterions, which stabilize [32] the $[Ru(phen)_3]^{2+}$ type cations more effectively, the greater their ionic radius. Thermal decomposition was always accompanied by an exothermic effect, due among other factors to mineralization of organic components liberated during pyrolysis of the examined compounds. Final temperatures of these processes varied between 785 and 980 °C. Ruthenium(IV) oxide was the final product of pyrolysis of the examined compounds except for $[Ru(phen)_3](VO_3)_2$, which underwent decomposition, similarly to $[Ru(bpy)_3](VO_3)_2$ [15,23], to a phase containing $Ru^{IV}$ and $V^{V}$ oxides. In the case of tris(phenanthroline)ruthenium(II) perrhenate, a decomposition intermediate was formed at 790 °C, viz. an alloy of composition $RuRe_2$, which was oxidized on further heating to $RuO_2$ and to $Re_2O_7$, which underwent sublimation.

## CONCLUSIONS

It follows from the experimental data presented in Table 2 and Fig. 1, and from previous investigations [14,15] that both phenanthroline and dipyridyl complexes of ruthenium(II) are characterized by relatively high initial decomposition temperatures. However, thermal stability of $[Ru(phen)_3]X_2$ type compounds is often higher than that of similar compounds of $[Ru(bpy)_3]X_2$ composition. The high pyrolysis temperatures of $[Ru(L{-}L)_3]X_2$ compounds indicate a strong Ru–N bond, stronger in $[Ru(phen)_3]X_2$ than in similar dipyridyl complexes. The various decomposition temperatures of ruthenium

TABLE 2

Results of thermal analysis

| No. | Complex | Temperature range of dehydration (° C) | Temperature (° C) |  | Decomposition product (mg) |  |
|---|---|---|---|---|---|---|
|  |  |  | At beginning of decomposition | At end of decomposition | Calc. | Found |
| **1** | $[Ru(phen)_3]Cl_2 \cdot 8H_2O$ | 55–170 | 345 | 900 | 15.5 | 15.4 $RuO_2$ |
| **2** | $[Ru(phen)_3]Br_2 \cdot 6.5H_2O$ | 55–190 | 395 | 910 | 14.5 | 14.4 $RuO_2$ |
| **3** | $[Ru(phen)_3]I_2 \cdot 3H_2O$ | 55–130 | 405 | 980 | 14.0 | 13.5 $RuO_2$ |
| **4** | $[Ru(phen)_3](ReO_4)_2 \cdot H_2O$ | 60–100 | 430 | 840 | 11.5 | 11.7 $RuO_2$ |
| **5** | $[Ru(phen)_3](VO_3)_2 \cdot 7H_2O$ | 50–200 | 330 | 785 | 32.6 | 31.2 $RuO_2 \cdot V_2O_5$ |
| **6** | $[Ru(phen)_3](SCN)_2 \cdot 3H_2O$ | 40–115 | 330 | 980 | 16.4 | 16.6 $RuO_2$ |

(II) phenanthroline complexes result from outer sphere interaction between anionic counterions and complex $[Ru(phen)_3]^{2+}$ cations [32].

It follows from the data listed in Table 2 that the dehydration temperatures of the synthesized ruthenium(II) complexes are lower than the corresponding initial decomposition temperatures. For this reason the compounds listed in the title can be readily obtained in an anhydrous state.

Tris(phenanthroline)ruthenium(II) perrhenate undergoes thermal decomposition in a way similar to the previously examined $[Ru(bpy)_3](ReO_4)_2$ [15,23]. An alloy of composition $RuRe_2$ is an intermediate in pyrolysis of both the compounds. On the basis of the obtained results and previous investigations [33], it might be anticipated that other metals forming complexes of $[M(L-L)_3]X_n$ type, where $n$ is the oxidation state of the metal M, would form rhenium alloys of stoichiometric composition $MRe_n$. This could evidently be a relatively simple method of obtaining at low temperature a number of alloys of rhenium, which is a refractory metal (m.p. 3180 ° C).

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