Section A -Research paper
ISSN 2063-5346

THE INTERACTION OF CHLORINE COMPOUNDS OF RHENIUM (RE IV) WITH ORTHONITROANIL COMPLEX COMPOUNDS AND THEIR THERMAL TRANSFORMATIONS

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Article History: **Received: 03.04.23** **Revised: 05.05.23** **Accepted: 20.06.23**

Abstract

İn recent years, the range of information about the chemistry of transition elements has expanded significantly. Thus, new types of complex compounds were synthesized, their structures were studied and unusual physico-chemical properties were revealed. Most of these compounds have found applications in various fields of industry and agriculture.

Among the transition elements located in D. İ Mendeleev's periodic table, the scope of the chemistry of complex compounds of rhenium, located in the additional subgroup of the seventh group, is wider and more colorful. Because, unlike other transition elements, it can show the degree of oxidation from -1 to +7 in its compounds. In addition, rhenium is known for its unusual physical and chemical properties, high melting temperature (318 °C), resistance to corrosion in various environments, etc. due to its properties, it is superior to other metals and is currently used in a number of important fields of modern technology.

İn the conducted research, a new complex combination of tetravalent rhenium with orthonitroaniline $[NO_2\text{-}C_6H_4NH_3]_2ReCI_6$ was synthesized, and their thermal transformations in the solid phase were studied by many thermogravimetric and İR spectroscopic methods. It was determined that Anderson grouping occurs first during heating, and then Re^{+4} is reduced to metallic rhenium as a result of the oxidation-reduction process.

İt is known from the literature that a number of compounds of rhenium, including complexes with organic donor bases, can be used as a starting material in obtaining oxide or metallic coatings, as well as as a catalyst in many organic synthesis processes. [1]

Despite the fact that there are enough materials in the literature about the synthesis and research of complex compounds of tetravalent rhenium with various amines [2-6] and phosphines [7, 8], there is very little information about its compounds with aromatic amines during the search.

In the presented article, the interaction of potassium hexahalogenorenate K_2ReX_6 ($X=CI^-$) with orthonitroaniline ($NH_2\text{-}C_6H_4\text{-}NO_2$) was studied and the physicochemical properties of the obtained complexes were studied.

Keywords: rhenium, physico-chemical properties, thermo gravimetric analyzes

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Practical part

Potassium hexahalogenorenate K_2ReX_6 ($X=CI^-$) was obtained by reducing 1 g of potassium perrhenate (KO_4Re) with 2 g of potassium iodide in 30 ml of strong hydrochloric or bromic acid according to the methodology written in the literature. [9]

Solid diortonitrophenylammonium hexachlororenate $[NO_2\text{-}C_6H_4\ NH_3]_2ReCI_6$ was obtained as a result of the reaction of orthonitroaniline with potassium hexachlororenate in hydrochloric acid medium:

$$K_2ReCI_6+(NH_2\text{-}C_6H_4\text{-}NO_2) \rightarrow [NO_2\text{-}C_6H_4NH_3]_2ReCI_6+2KCI$$

Orthonitroaniline ($NH_2\text{-}C_6H_4\text{-}NO_2$) previously dissolved in acetone was added to the obtained yellowish-green solution after complete dissolution of 3g of K_2ReCI_6 in 30 ml of solid hydrochloric acid at 60-70°C with constant stirring using a magnetic stirrer (exceeding the

ISSN 2063-5346

stoichiometric amount). At this time, the color of the solution has turned dark yellow. After heating the solution at the specified temperature for 20-25 minutes without stopping the mixing process, it was filtered through a Schott filter and allowed to crystallize. After about 25-30 minutes, small dark green crystals began to precipitate from the solution. The obtained crystals were filtered and dried in a desiccator over sulfuric acid until constant weight (table 1.)

Table 1. Elemental analysis of the obtained substances.

№	Combinations	Color	Output in %	% Found			In theoretical %		
				Re	X	N	Re	X	N
1	$[NO_2–C_6H_4\text{-}NH_3]_2ReCI_6$	Light green	86	28,15	31,88	8,86	27,47	31,5	8,27

Table 2. Results of thermo gravimetric analyzes of the studied complex.

№	Combinations	Temperature range, oC	T_{mek}, ^oC	mass loss, %		Decomposition product	
				Find out	Calculated	Detached	Remainder
1	$[NO_2–C_6H_4\text{-}NH_3]_2ReCI_6$	100-180 180-270 270-530	150 240 500	12 40,5 20,5	11 41 21	- 2 HCl $(NO_2–C_6H_4\text{-}NH_3)_2$ - 2 Cl_2	$ReCl_4[NO_2–C_6H_4\text{-}NH_3]_2$ $ReCl_4$ Re

Discussion of results

The results of thermogravimetric studies are given in table 2 in pictures 1 and 2 from the thermogravigram of the studied substances in air.

As can be seen from Figure 1 and Table 2, $[NO_2\text{-}C_6H_4\ NH_3]_2ReCI_6$ undergoes Anderson grouping by losing two moles of hydrogen chloride in the temperature range of 100-180°C, and as a result, orthonitroaniline deprotonates and moves from the outer sphere to the inner sphere. At this time, according to the values of the TQ-curve, the mass loss was 12%, which fully corresponds to the theoretical calculations according to the following reaction equation.

$$[NO_2\text{-}C_6H_4\ NH_3]_2ReCI_6 \xrightarrow{100-180^{\circ}D} ReCI_4(NO_2\text{-}C_6H_4\ NH_3)_2 + 2HCI$$

A sharp decrease in mass in the TQ curve occurs in the temperature range of 180-270°D. (40.5%), which is accompanied by a strong exothermic effect, and as a result, the complex is completely destroyed by amine:

Based on the results of thermo gravimetric studies, the decomposition process can be imagined as follows.

$$[NO_2\text{-}C_6H_4\text{-}NH_3]ReCI_6 \xrightarrow[-2HCl]{100–180^{\circ}C} ReCI_4(NO_2\text{-}C_6H_4\text{-}NH_3)_2$$

$$\xrightarrow[-(NO_2-C_6H_4-NH_3)_2]{180–270^{\circ}C}$$

$$ReCI_4 \xrightarrow[-2Cl_2]{270–530^{\circ}C} Re \xrightarrow{hava,530–1000^{\circ}S} Oxides$$

of rhenium (volatiles)

As can be seen from the diagram, the final product of the fission process is metallic rhenium.

ISSN 2063-5346

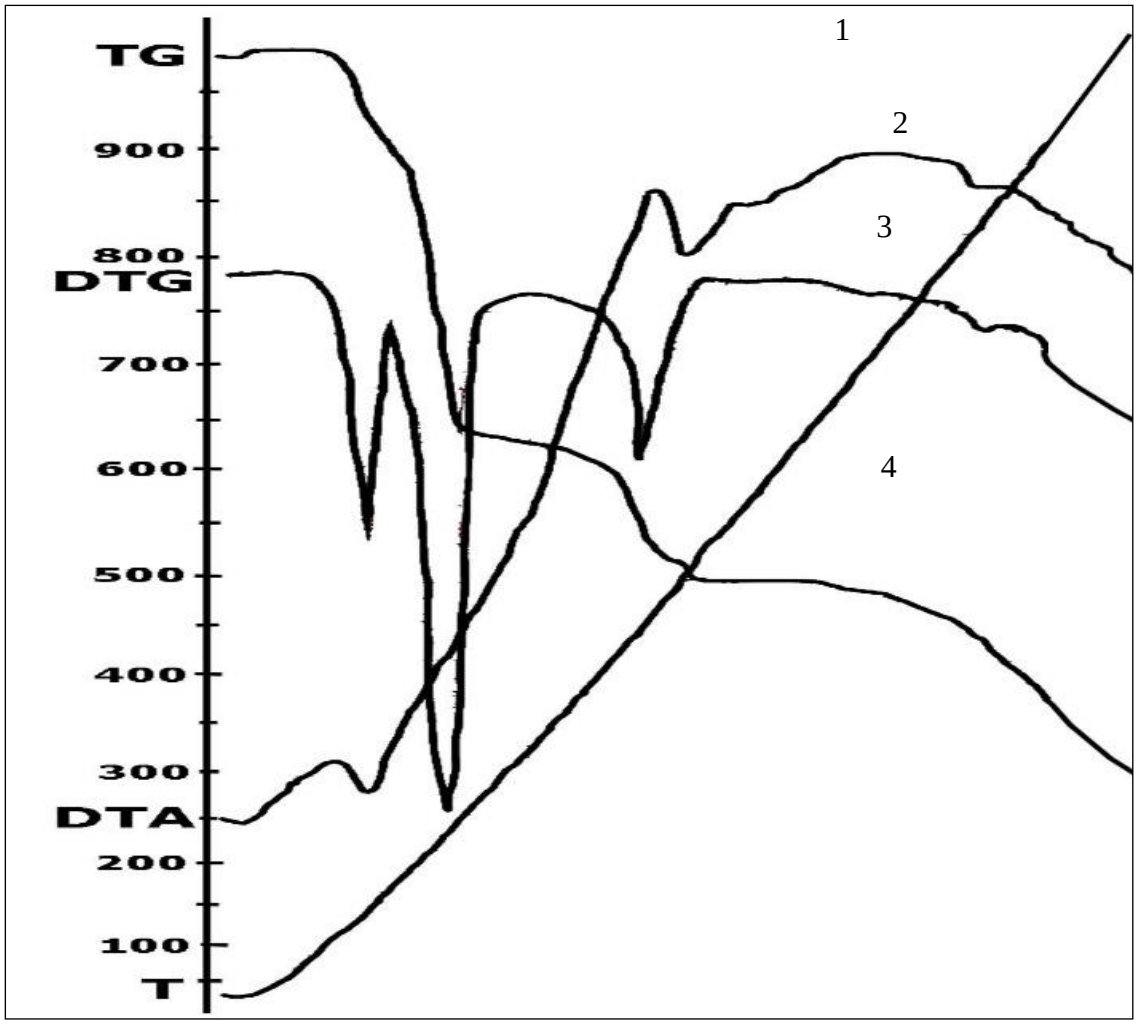

Figure 1. Thermogravigram of -[NO_2-C_6H_4 NH_3]$_2$$ReCI_6$.

1.-temperature change (T); 2-mass differential change curve (DTC); 3-differential curve of temperature change (DTA); 4-mass change (TQ).

In order to determine the nature of orthonitroaniline coordination in the synthesized substances, their IR absorption spectra were studied. The obtained compounds (Fig. 3.). IR-spectra of [NO_2-C_6H_4-NH_3]$ReCI_6$, $ReBr_4$(NO_2-C_6H_4-NH_3)$_2$ and orthonitroaniline decomposition products are given in figure 3.

As can be seen from Figure 3, the absorption bands characteristic of orthonitroaniline are clearly visible with some changes in the spectra of both the obtained substances and the decomposition products. If you look closely at Figure 3, it becomes clear that when orthonitroaniline is protonated in an acidic environment and enters the composition of the compound in the form of a cation (Figure 3 b.), the absorption band at the frequency of 3500 cm-1, which is characteristic of the N-H bond, is completely lost, and instead it is at 2500-2700 in the spectrum of the chlorinated derivative. Absorption bands with several maxima are formed in the cm-1 frequency domain.

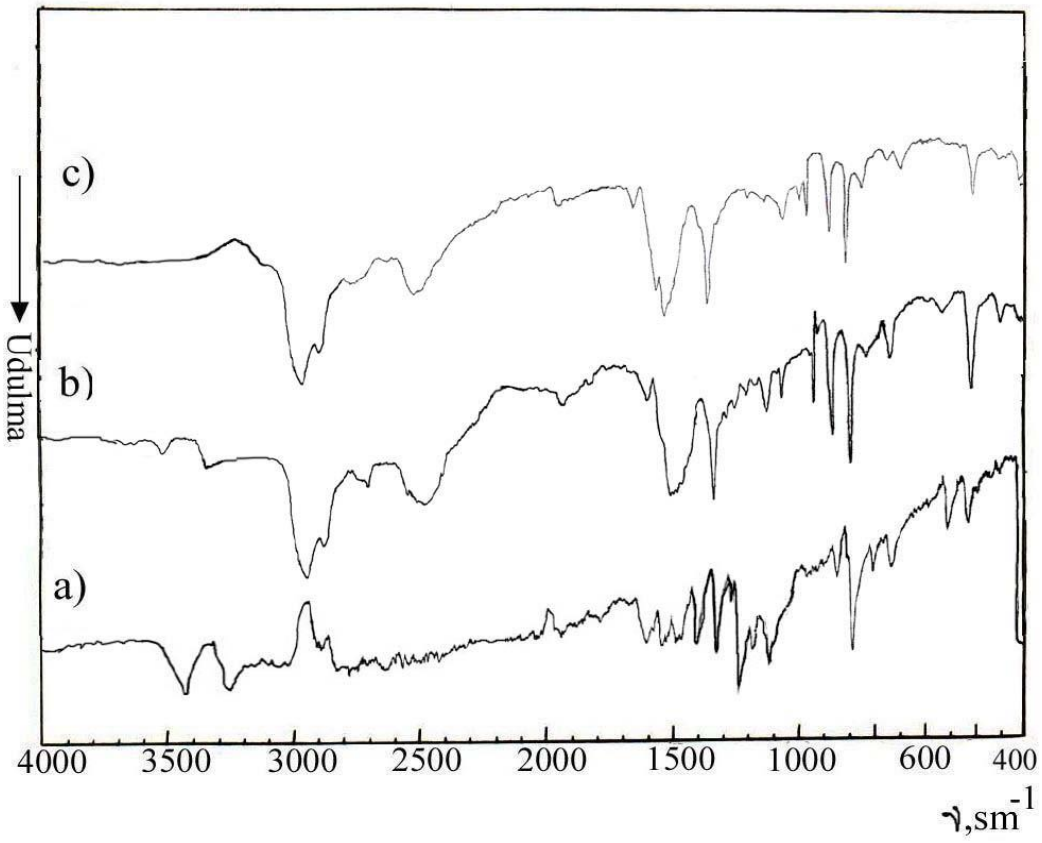

Figure 3. IR spectra of compounds
a) NH_2-C_6H_4-NO_2
b) $[NO_2$-C_6H_4 $NH_3]_2ReCI_6$
c) $ReBr_4[NO_2$-C_6H_4-$NH_3]_2$

This, it was determined by the thermogravimetric method that the studied substances begin to decompose at 100°C, and this process ends with obtaining metallic rhenium at 565°C.

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