DOI: 10.6060/ivkkt.20216401.6161

УДК: 546.719.057

КЛАСТЕРНЫЕ КОМПЛЕКСЫ РЕНИЯ С КАРБОНИЛЬНЫМИ И АМИНОВЫМИ ЛИГАНДАМИ

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Разработаны методы синтеза кластерных комплексов рения на основе карбонильных и аминсодержащих органических бифункциональных лигандов. Структура и строение полученных комбинаций кластеров были определены на основании данных ИК-спектроскопии, методами термогравиметрии и элементного анализа. Образцы лигандов I и II были получены конденсацией хлорангидридов циклопентан- и циклогексанкарбоновых кислот с этиленом с последующей заменой атома хлора аминными группами. Для получения кластерных комплексов рения с синтезированными лигандами заранее был приготовлен ультрадисперсный раствор рения в дистиллированной воде. С этой целью соль треххлористого рения ($ReCl_3$) растворялась в воде и к полученному раствору при энергичном перемешивании добавлялось порциями рассчитанное количество боргидрида натрия в атмосфере азота. Быстро возникающие черно- дисперсные наночастицы металлического рения не осаждались. При прибавлении органических лигандов I и II образовались соответствующие кластерные соединения III и IV, которые постепенно в течение 30 мин, осаждались из водного раствора. Полученные черно-коричневые осадки промывались дистиллированной водой и сушились в атмосфере азота при температуре 35-40 °C. Определены температуры плавления синтезированных соединений, составляющие для кластера III- 195 °C и кластера IV- 212 °C (с разложением). В ИК спектрах кластерных соединений обнаружены интенсивные полосы поглощений, характеризующие наличие как кетонной карбонильной группы, так и аминного фрагмента. Полосы поглощений кетонных групп в кластерных соединениях по сравнению с исходными лигандами смещаются в сторону высоких частот. Аналогичная картина наблюдается и при сравнении ИК- колебаний C-N связей в исходных лигандах и соответствующих кластерных соединениях. Результаты элементного анализа подтверждают структуры кластерных соединений и вполне согласуются с представлениями о том, что при восстановлении солей рения гидридами металлов в водном растворе образуются кластерные соединения. По-видимому, в данном случае образуются наиболее устойчивые кластеры рения, имеющие тетраэдрическую структуру. Термогравиметрический анализ позволил установить наличие пика при температуре 318 °C с массовым числом 744,8 у.е., соответствующего кластерному сочетанию четырех атомов рения. На каждом этапе разложения экспериментальные потери массы хорошо согласуются с вычисленными значениями.

Ключевые слова: синтез, рений, кластерные комплексы, амин и карбонил содержащие лиганды, бифункциональные лиганды, циклопентиламинокетон, циклогексиламинокетон

CLUSTER COMPLEXES OF RHENIUM WITH CARBONYL AND AMINE CONTAINING LIGANDS

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Methods for the synthesis of rhenium cluster complexes based on carbonyl and amine containing organic bifunctional ligands have been developed. The structure of the obtained cluster combinations were determined on the basis of IR spectroscopy data, methods of thermogravimetry and elemental analysis. Samples of ligands I and II were obtained by condensation of cyclopentane and cyclohexane carboxylic acids chloroanhydrides with ethylene, followed by the replacement of the chlorine atom by amine groups. To obtain cluster complexes of rhenium with the synthesized ligands, an ultradisperse solution of rhenium in distilled water was prepared in advance. To this end, the rhenium trichloride salt ($ReCl_3$) was dissolved in water and the calculated amount of sodium borohydride in a nitrogen atmosphere was added in portions to the resulting solution with vigorous stirring. Rapidly arising black dispersed nanoparticles of metallic rhenium were not deposited. When organic ligands I and II are added, the corresponding cluster compounds III and IV are formed, which gradually over 30 minutes. precipitated from aqueous solution. The resulting black-brown precipitates were washed with distilled water and dried in a nitrogen atmosphere at a temperature of 35-40 °C. The melting points of the synthesized compounds are determined, which are components for cluster III-195 °C and cluster IV- 212 °C (with decomposition). In the IR spectra of cluster compounds, intense absorption bands were found, which characterize the presence of both a ketone carbonyl group (1718 sm^{-1}, 1720 sm^{-1}) and an amine fragment (2727 sm^{-1}, 2720 sm^{-1} and 2613 sm^{-1}, 2609 sm^{-1}). The absorption bands of ketone groups in cluster compounds are shifted toward higher frequencies compared to the initial ligands. A similar picture is observed when comparing IR vibrations of C – N bonds in the initial ligands and the corresponding cluster compounds. The results of elemental analysis confirm the structure of cluster compounds and are in complete agreement with the notion that the reduction of rhenium salts with metal hydrides in an aqueous solution forms cluster compounds. Apparently, in this case, the most stable rhenium clusters with a tetrahedral structure are formed. Thermogravimetric analysis made it possible to establish the presence of a peak at a temperature of 318 °C with a mass number of 744.8 c.u. corresponding to the cluster combination of four rhenium atoms. At each stage of decomposition, the experimental mass loss agrees well with the calculated values.

Key words: synthesis, rhenium, cluster complexes, amine- and carbonyl containing complexes, cyclopentyl amino ketone ligand, cyclohexyl amino ketone ligand

Для цитирования:

Агагусейнова М.М., Гудратова Ф.Д. Кластерные комплексы рения с карбонильными и аминовыми лигандами. *Изв. вузов. Химия и хим. технология*. 2021. Т. 64. Вып. 1. С. 47–51

For citation:

Agahuseynova M.M., Gudratova F.D. Cluster complexes of rhenium with carbonyl and amine containing ligands. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* [ChemChemTech]. 2021. V. 64. N 1. P. 47–51

INTRODUCTION

The development of Inorganic chemistry in the XX-th century was accompanied by remarkable discoveries. Increasingly, complex compounds, in the molecules of which contain several metal ions – the so-called polynuclear coordination compounds, where the bond length between metal atoms is markedly shortened compared with compact metals, have begun to fall into the field of vision of nonorganic chemists. In contrast to the classical single-site coordination compounds, here the ligands are surrounded by several atoms (ions) of metals, which are closely related to each other. Initially, such polynuclear complexes included $Ta_6Cl_{14}·7H_2O$, $MoCl_2$ and some of its derivatives. An interesting fact is that as early as 1943, the polynuclear complex compound Rh_4CO_n was obtained by carbonylation of anhydrous Rh_4Cl_3 [1]. In 1963, the structure of rhenium chloride was established, in which rhenium atoms form a triangle with short Re-Re distances equal to just 2.47 A^0 [2]. The discovery of antitumor activity and a unique low toxicity and a fairly wide range of biological activity distinguish rhenium complexes from their analogues [3-4, 5-7]. A characteristic feature of compounds containing polyvalent transition metal atoms is the formation of cluster compounds. In recent years, the chemistry of cluster compounds of transition metals, including rhenium, is one of the most rapidly developing areas of modern inorganic chemistry [8-17].

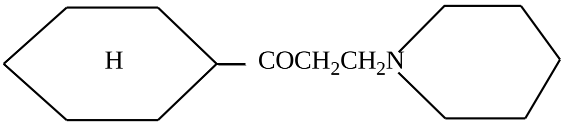
Despite the existing progress made in the cluster chemistry of transition metals, until recently the halide and chalcogenide containing complexes were most widely studied, the nitrogen-containing complexes were considered to a lesser extent. While Mo- and W- have accumulated a fairly extensive material, the cluster chemistry of rhenium has big problems. In this regard, it was of interest to obtain polynuclear metal complexes of rhenium with organic bifunctional ligands and study of their structure and properties [18-21].

This paper is devoted to the synthesis of cluster compounds with carbonyl and amine-containing organic bifunctional ligands. The structures of the synthesized cluster compounds were studied by the methods of elemental analysis, IR spectroscopy and thermogravimetric analysis.

EXPERIMENTAL PART

These ligands were synthesized according to the procedure described in [14, 22-24]. Samples of ligands I and II were obtained, respectively, by the condensation of cyclopentane - and cyclohexane chloroanhydrides of carboxylic acids with ethylene, followed by the replacement of the chlorine atom by amine groups.

I – 1-cyclopentyl-3-(piperidin-1yl) propan-1-one



II – 1-cyclohexyl-3-(piperidin-1yl) propan-1-one

The names of these synthesized ligands are given in conformity with IUPAC systems [25, 26].

The purity of these ligands is determined by gas-liquid chromatography.

To obtain a rhenium cluster complex with the aforementioned ligands, we have previously prepared an ultradisperse solution of rhenium in distilled water. To this end, 0.775 g (0.001 mol) of rhenium trichloride was dissolved in 50 ml of distilled water. To the resulting solution with vigorous stirring in portions for 40 s added 0.114 g (0.001 mol) of sodium borohydride. After cessation of gas evolution (H_2 and BH_3), 0.209 g (0.001 mol) of amino ketone I was added to the reaction mixture with vigorous stirring. After the completion of the reaction, stirring was continued for another 20 min. On standing, 0.67 g of black brown crystals of cluster complex III with m.p. fell out. 195 °C (decomposition at melting). Found, %: Re – 46.89; C – 39.20; H – 6.2; N – 3.47 $Re_4C_{52}H_{92}O_4N_4$. Calculated, %: Re – 47,12; C – 39.47; H – 5.82; N – 3.54.

Using a similar procedure, cluster compound IV was obtained, yield 47%, m.p. 212 °C (melts with decomposition).

Found, %: Re – 45.2; C – 39.9; H – 6.23; N 3.53.

$Re_4C_{56}H_{100}O_4N_4$. Calculated, %: Re – 45.5; C – 41.06; H – 6.11; N – 3.42.

Elemental analysis for C, H, N was performed on a Carlo Erba 1106 and Vario EL instrument. IR spectra were recorded on a Bruker IFS-85 Fourier spectrometer (tablets with KBr)

Thermograms of cluster compounds III and IV were obtained using the “Netzsch” apparatus STA 449 F3 Yupiter.

RESULTS AND DISCUSSION

The structures of the obtained compounds III and IV were determined on the basis of the data of IR spectral analysis, thermogravimetry and elemental analysis. In the IR spectrum of compounds III and IV, intense absorption bands were detected at 1718 sm^{-1} and 1720 sm^{-1}, respectively, characterizing the presence of the ketone carbonyl group.

The absorption bands at 2727 sm^{-1} and 2720 sm^{-1} correspond to the amine fragment in compound III. The absorption bands of 2613 sm^{-1} and 2609 sm^{-1} characterize the presence of the amine group in cluster compound IV.

So, if in the initial ligands I and II the absorption bands of the ketone carbonyl group are 1712 sm^{-1} and 1714 sm^{-1}, then in the cluster substances III and IV the absorption bands of these groups appear at 1718 sm^{-1} and 1720 sm^{-1}, respectively. A certain regularity is observed when comparing IR vibrations of C – N bonds in the initial I, II ligands and in the corresponding cluster compounds III and IV. So, if in the initial ligands the absorption bands of C–N bonds appear at 2727 sm^{-1} and 2720 sm^{-1}, then in the corresponding clusters III and IV these oscillations are 2613 sm^{-1} and 2609 sm^{-1}.

In the thermogravimetric analysis of these compounds, a “peak” was found at a temperature of 318 °C with a mass number of 744.8 c.u., corresponding to a cluster combination of four rhenium atoms. It should be noted that the absorption bands of ketone groups in the starting ligands I and II are markedly reduced when comparing these substances as part of cluster compounds. Thermogravimetric method also found that compounds III and IV are stable to a temperature of 187 °C and 201 °C, respectively, above these temperatures, release of amino ketones I and II occurs, accompanied by endothermic effects in the range 177-229 °C with maxima at 195 °C and 209 °C, respectively. The experimental and calculated molecular weight loss for clusters III and IV is 20.40% and 21.09%, respectively.

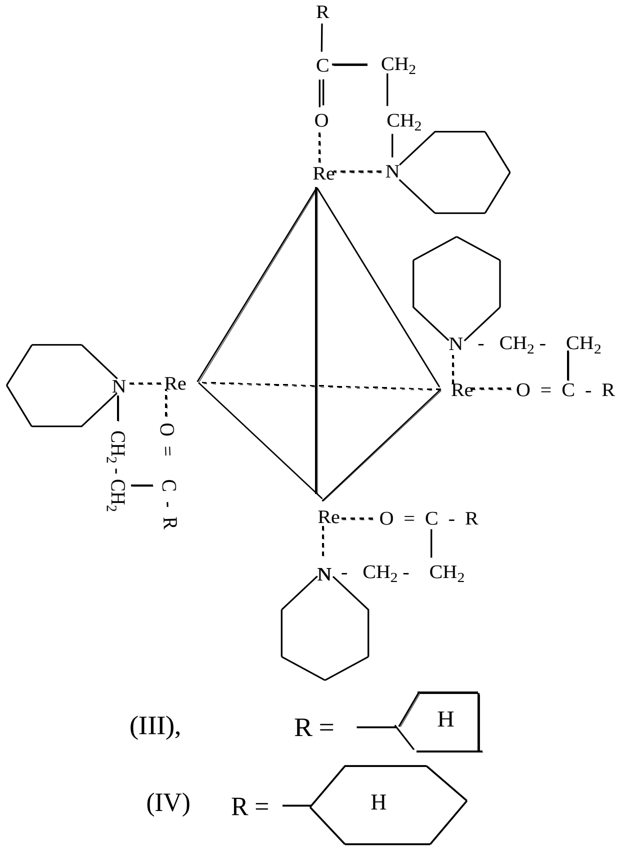


Figure. The structure of the synthesized complex compounds of rhenium with 1-cyclopentyl-3-(piperidin-1yl) propan-1-one (III) and 1-cyclohexyl-3-(piperidin-1yl) propan-1-one (IV)
Рисунок. Строение синтезированных комплексных соединений рения с 1-циклопентил-3- (пиперидин-1-ил) пропан-1-оном (III) и 1-циклогексил-3- (пиперидин-1-ил) пропан-1-оном (IV)

After complete removal of the amino ketone I at a temperature of 650 °C, the mass according to the thermogravimetric data of rhenium was 79.2%. The theoretically calculated mass loss is 78.89%. At each stage of decomposition, the experimental mass loss agrees well with the calculated values. A similar method was used to analyze cluster compound IV. The results obtained are quite consistent with the assigned composition.

The results of elemental analysis also confirm the attributed structures of cluster compounds III and IV. The experimental data obtained by us are in complete agreement with the ideas that, during the reduction of rhenium salts by hydrides of elements in an aqueous solution, clusters of rhenium atoms arise.

Apparently, the most stable among them is the metal cluster Re_4, which has a tetrahedral structure.

CONCLUSIONS

Method of synthesis of rhenium cluster complexes based on carbonyl and amine containing organic bifunctional ligands have been developed.

It was established that during the reduction of rhenium salt in an aqueous solution, ultra-dispersed nano-particles of metallic rhenium, are formed which interacting with β-amino ketones results to formation of clusters complexes.

Structure of the obtained clusters has been determined on the basis of data of element analysis, IR-spectroscopy and thermogravimetric investigations.

It has been revealed that rhenium has tetrahedral coordination in the synthesized cluster complexes.

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Поступила в редакцию 15.11.2019
Принята к опубликованию 29.10.2020

Received 15.11.2019
Accepted 29.10.2020