

SYNTHESIS AND APPLICATION OF ACETYL ACETONATE COMPLEXES OF TRIVALENT RHENIUM (RE(III)) WITH METAL-METAL COMPOUNDS

F.A. Amirli¹, O.M. Gulalov², Sh.İ. Kahramanova³, N.M. Shixaliyev⁴, P.V. Aliyeva⁵

^{1,2} Azerbaijan State Oil and Industry University, Baku, Azerbaijan

^{3,4,5} Institute of Catalysis and Inorganic Chemistry named after Academician M. Nagiyev, Baku, Azerbaijan

¹ fariz.emirov@asoiu.edu.az, <http://orcid.org/0000-0002-9095-2982>

² omar.gulalov@mail.ru, <http://orcid.org/0000-0003-0555-374X>

³ sahnaz.qehremanova@mail.ru, <http://orcid.org/20000-0001-7955-4118>

⁴ nshkh02@bk.ru, <http://orcid.org/0009-0005-2542-2220>

⁵ piraneeliyeva@gmail.com, <http://orcid.org/0009-0006-5763-7311>

ABSTRACT

Dinuclear acetylacetonate derivatives of trivalent rhenium were obtained and their physicochemical and thermal properties were studied in detail. The composition and type of compounds were determined using chemical, IR-spectral and X-ray phase methods from various analytical methods. During the study of the proposed structures of the obtained compounds by IR spectral analysis, it was determined that the absorption spectra of ion complexes containing protonated amines are almost identical to each other. It was determined that there are intense bands at 1380 and 1460 cm^{-1} , which are characteristic of symmetric and asymmetric bending vibrations of methyl groups, respectively. In addition, in the high-frequency region of the spectra, the presence of broad intense bands in the region of 3050-3250 cm^{-1} with several maxima characteristic of stretching vibrations of protonated amines was revealed. Thermogravimetric methods have determined that they decompose at low temperatures and that in all cases the final solid phase product is rhenium metal. As a result of many interesting studies, it was determined that many representatives of this class of compounds can be used as starting products for the production of effective catalysts in obtaining oxide or metal coatings and in many organic synthesis processes.

Keywords: complex, analysis, synthesis, temperature, ligand, solution.

Introduction

Complexes with β -diketones were obtained for many metals [1, 2]. These are mainly dinuclear and polynuclear complexes without metal-metal bonds. Only dinuclear β -diketonates with a metal-metal bond are known for rhodium [3-6].

At present, there is very little information in the literature about the synthesis and research of rhenium (III) β -diketonate complexes with multiple metal-metal bonds. Nevertheless, they can be of great practical interest, since many representatives of this class of compounds can be used as starting products for the production of effective catalysts in obtaining oxide or metal coatings and in many organic synthesis processes.

The purpose of the conducted research is to study the interaction of dinuclear rhenium (III)

complexes with acetylacetone.

Experimental part

Infrared (IR) spectra were recorded in the 400-4000 cm^{-1} region on UR-20 and SPECORD-M 80 spectrometers.

Before imaging, samples were prepared as a suspension in liquid paraffin. In some cases, test substances are compressed into potassium bromide tablets.

Differential thermogravimetric analysis was carried out in the Q-1500 D derivatography of the Paulik-Edrey-Paulik system using a platinum-platinum-rhodium thermocouple in a nitrogen atmosphere in the temperature range of 20-900°C. The heating rate of the oven is 10 degrees/min. Calcined alumina was used as standard. Ceramic vessels served as containers for samples. Accuracy of temperature determination is 5°C, weight loss is 0.001 g.

The starting compounds $\text{M}_2[\text{Re}_2\text{X}_8]$ with $\text{M}=\text{K}^+$ used in the work were obtained by us for the first time according to the method described in [7] and $\text{M}=(\text{C}_2\text{H}_5)_3\text{NH}^+, (\text{CH}_3)_2\text{NH}_2$.

Synthesis of triethylammonium octabromorelate $[(\text{C}_2\text{H}_5)_3\text{NH}]_2[\text{Re}_2\text{Br}_8]$.

A sample (0.5 g) of $\text{K}_2[\text{Re}_2\text{Br}_8]$ was dissolved in 50 mL of concentrated bromic acid in a reflux condenser flask with continuous stirring at 60-70°C under a stream of inert gas.

The resulting brown solution is cooled to room temperature, then filtered and an excess of triethylamine, previously dried over calcium chloride, is added. Then the solution was heated again at 50-60°C for 15 minutes and allowed to crystallize. Well-formed dark brown crystals precipitated from the solution within 30 min, which were filtered, washed with mother liquor, several times with ether, and dried in a desiccator over sulfuric acid until a stable mass was formed. Yield 95% (Table 2. link 2).

Table 1. Results of the chemical analysis of the obtained complexes.

№	Mixed	Colour	Exit	% found				Calculated %			
				Re	X	N	C	Re	X	N	C
1	$[(\text{CH}_3)_2\text{NH}]_2[\text{Re}_2\text{Br}_8]$	Brown	95%	33,8	58,3	2,6	4,85	33,6	57,97	2,5	4,34
2	$[(\text{C}_2\text{H}_5)_3\text{NH}]_2[\text{Re}_2\text{Br}_8]$	Brown	90%	31,2	50,0	2,6	10,2	30,7	52,5	2,3	11,8
3	$\text{Re}_2\text{Cl}_4(\text{C}_5\text{H}_7\text{O}_2)_2$	Green	96%	52,2	19,9	-	1,3	52,4	19,94	-	16,8

Synthesis of dimethylammonium octachloronate $(\text{CH}_3)_2\text{NH}_2)_2[\text{Re}_2\text{Br}_8]$.

Weighed (0.5 g) $\text{K}_2[\text{Re}_2\text{Br}_8]$ was dissolved in 40 ml of bromic acid in a flask with a reflux condenser at 80°C under a stream of inert gas. The resulting solution is cooled, filtered and an excess of dimethylamine is added. Then it was heated at 50°C for 15-20 minutes and allowed to crystallize. Well-formed crystals precipitated from the solution within 1 h, which were filtered, washed several times with ether and mother liquor, and dried in a desiccator over sulfuric acid until a stable mass was formed. Yield 93% (Table 1. link 1).

Other octahalide complexes listed in Table 1 were obtained by a similar method.

Synthesis of tetrachlorodiacetylacetonadiriium $\text{Re}_2\text{Cl}_4(\text{C}_5\text{H}_7\text{O}_2)_2$ – was carried out in two ways.

In the first method, a weight of $[(\text{CH}_3)_2\text{NH}_2]_2[\text{Re}_2\text{Cl}_8]$ (0.3g) was dissolved in 35 ml of

acetone in a reflux condenser flask with constant stirring and at 50-60°C until complete dissolution. Then the obtained solution is cooled to room temperature, filtered and 15-20 ml of acetylacetone is added. At the same time, the color of the solution constantly changed from blue to greenish-blue. A blue-green crystalline precipitate precipitated from the solution in about 2-3 hours, filtered, washed with mother liquor, several times with ether, and dried in a desiccator over sulfuric acid until a stable mass was formed. Yield 96% (Table 1. link 3).

The remaining octahalide complexes were also used as starting compounds to prepare the mixed ligand acetylacetonate complex, and in all cases the results were identical.

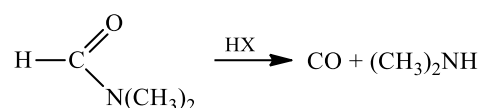
In the second method, it was carried out by isothermal heating of the complex $\text{Re}_2\text{Cl}_4(\text{C}_5\text{H}_7\text{O}_2)_2(\text{DMFA})_2$. For this purpose, the derivatogram of the dimethylformamide derivative (Figure 1) was recorded and the onset of thermal decomposition was determined.

The drawn $\text{Re}_2\text{Cl}_4(\text{C}_5\text{H}_7\text{O}_2)_2(\text{DMFA})_2$ is heated in a nitrogen flow in a porcelain vessel at a temperature of 160-170°C for 3.5-4 hours. At the same time, the color of the product changed from blue to bright green. The identity of the resulting product with the compound $\text{Re}_2\text{Cl}_4(\text{C}_5\text{H}_7\text{O}_2)_2$ is confirmed by chemical and IR spectral analysis methods.

Results and its discussion

The proposed structures of the obtained compounds were investigated by IR spectral analysis. The absorption spectra of ion complexes containing protonated amines (tables 1-4) are almost identical. Thus, there are intense bands characteristic for symmetric and asymmetric bending vibrations of methyl groups at 1380 and 1460 cm^{-1} , respectively. In addition, in the high-frequency region of the spectra, broad intense bands appear in the region of 3050-3250 cm^{-1} with several maxima characteristic of stretching vibrations of protonated amines.

It is interesting that during the synthesis of complexes $[(\text{CH}_3)_2\text{NH}_2]_2[\text{Re}_2\text{Cl}_8]$ We used dimethylformamide as a donor base. However, the IR spectra of these compounds do not have absorption bands characteristic of carbonyl groups. Thus, it was determined that under the reaction conditions, dimethylformamide molecules are decarbonylated to form dimethylamine.



The resulting dimethylamine is then protonated and incorporated as a cation.

In this study, the thermal decomposition of the synthesized complexes was studied. Data on the thermal decomposition of the studied compounds are given in Table 2.

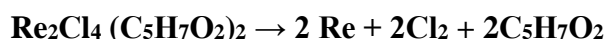
Derivatograms recorded in nitrogen flow are shown in Fig. 1 and 2.

Table 2. Data on the thermal decomposition of rhenium (III) acetylacetonate complexes.

Mixed.	Temperature range, °C	Decomposition product	
		Remainder	To sublimate
$\text{Re}_2\text{Cl}_4(\text{C}_5\text{H}_7\text{O}_2)_2$ (DMFA) ₂	120-180 350-430	$\text{Re}_2\text{Cl}_4(\text{C}_5\text{H}_7\text{O}_2)_2$ Re.	DMFA $\text{C}_5\text{H}_7\text{O}_2$, Cl_2
$\text{Re}_2\text{Cl}_4(\text{C}_5\text{H}_7\text{O}_2)_2$	320-380 470	ReBr_2 Re.	$\text{C}_5\text{H}_7\text{O}_2$ Br_2

According to the DTG curve (Fig. 2), the decomposition of the complex $\text{Re}_2\text{Cl}_4(\text{C}_5\text{H}_7\text{O}_2)_2$ (DMFA)₂ occurs at 180°C and two molecules of dimethylformamide are removed. After that, the process continues in the same way $\text{Re}_2\text{Cl}_4(\text{C}_5\text{H}_7\text{O}_2)_2(\text{DMFA})_2$ (Figure 2). Thus, during the thermal decomposition of $\text{Re}_2\text{Cl}_4(\text{C}_5\text{H}_7\text{O}_2)_2(\text{DMF})_2$, dimethylformamide molecules are first removed, then the main thermal destruction of the complex occurs with the formation of metal rhenium.

As can be seen in the coupling thermogram, $\text{Re}_2\text{Cl}_4(\text{C}_5\text{H}_7\text{O}_2)_2$ (Fig. 2.) a clear endothermic effect is observed at 345°C, which corresponds to the removal of two molecules of acetylaceton. In addition, the decomposition of the complex is accompanied by a smooth decrease in the TG curve without a clear effect on the DTA curve. Therefore, it turned out that it was not possible to determine the mass loss threshold corresponding to the volatile products. Accordingly, the total mass loss corresponding to the values calculated from this reaction was calculated:



Thus, intramolecular redox processes occur during the thermal decomposition of dinuclear β -diketonate complexes of rhenium (III) with a short metal-metal bond, which is accompanied by the reduction of rhenium (III) to metal.

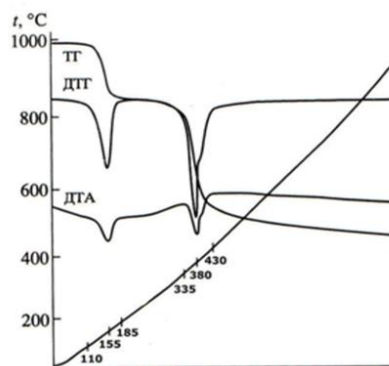


Figure 1. Derivatogram $\text{Re}_2\text{Br}_4(\text{C}_5\text{H}_7\text{O}_2)_2(\text{DMFA})_2$.

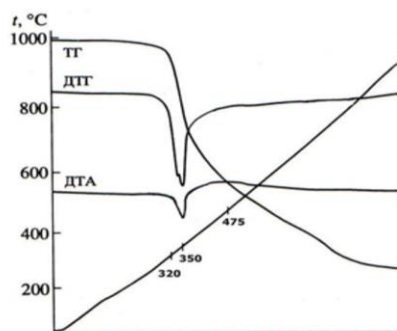


Figure 2. Derivatogram $\text{Re}_2\text{Cl}_4(\text{C}_5\text{H}_7\text{O}_2)_2$.

References

1. Проблемы химии и применение β -дикетонатов металлов. Подю ред. Спицына В.И.- М.: «Наука», 1982, с.263.
2. Теоретическая и прикладная химия β -дикетонатов металлов. – Под.ред. Спицына В.И.- М.: «Наука», 1985, 270 с.
3. Барановский И.Б., Жиляев А.Н., Дикарева Л.М. // Ж. Неорган химии., - 1988, Т.33, №12. с.3123-3128.
4. Дикарева Л.М., Андрианов В.И., Жиляев А.И.Б., Барановский И.Б. // Ж. Неорган. Химии, - 1989, Т.34, №2, с.391-394.
5. Mc Carthy H.Y., Tocher D.A. // Polyhedron, - 1989, vol. 8, p.1117-1121.
6. Mc Carthy H.Y., Tocher D.A. // Inorg. Chim. Acta, - 1988, vol.145, p.171-173.
7. Лебедев В.Г., Котельникова А.С., Мисаилова Т.В. – В сб. : Рений. Химия, технология, анализ. /Тр. IV Всес. сов. по проблеме рения /.- М.: Наука, 1976, С. 27-31.

ÜÇVALENTLİ RENIUMUN (RE(III)) ASETİL ASETONAT KOMPLEKSLƏRİNİN METAL-METAL BİRLƏŞMƏLƏRİ İLƏ SİNTEZİ VƏ TƏTBİQİ

F.Ə.Əmirli¹, Ö.M.Gülalov², Ş.İ.Qəhrəmanova³, N.M.Şıxəliyev⁴, P.V.Əliyeva⁵

^{1,2}Azərbaycan Dövlət Neft və Sənaye Universiteti, Bakı, Azərbaycan

^{3,4,5} Akademik M.Nağıyev adına Kataliz və Qeyri-üzvi Kimya İnstitutu, Bakı, Azərbaycan

¹ fariz.emirov@asoiu.edu.az, <http://orcid.org/0000-0002-9095-2982>

² omar.gulalov@mail.ru, <http://orcid.org/0000-0003-0555-374X>

³ sahnaz.qehremanova@mail.ru, <http://orcid.org/20000-0001-7955-4118>

⁴ nshkh02@bk.ru, <http://orcid.org/0009-0005-2542-2220>

⁵ piraneeliyeva@gmail.com, <http://orcid.org/0009-0006-5763-7311>

XÜLASƏ

Üçvalentli reniumun ikinüvəli asetilaseton törəmələri alınmış və onların fiziki-kimyəvi və istilik xassələri ətraflı öyrənilmişdir. Müxtəlif analitik, kimyəvi, İQ-spektroskopiya və rentgen faza üsulları ilə alınan birləşmələrin tərkibi və quruluşu müəyyən edilmişdir. Alınan birləşmələrin təklif olunan quruluşunun İQ-spektral analizi ilə tədqiqi zamanı müəyyən edilmişdir ki, tərkibində protonlaşmış aminlər olan ion komplekslərinin udma spektrləri bir-biri ilə demək olar ki, eynidir. Müəyyən edilmişdir ki, 1380 və 1460 sm^{-1} -də metil qruplarının müvafiq olaraq simmetrik və asimmetrik deformasiya vibrasiyaları üçün xarakterik olan intensiv zolaqlar mövcuddur. Bundan əlavə, spektrlərin yüksək tezlikli bölgəsində 3050-3250 sm^{-1} bölgəsində protonlanmış aminlərin valent vibrasiyaları üçün xarakterik olan bir neçə maksimuma malik geniş intensiv zolaqların olması aşkar edilmişdir. Termoqravimetrik üsullar vasitəsilə bu birləşmələrin aşağı temperaturda parçalandığını və bütün hallarda qalıq bərk faza məhsulunun renium metal olduğunu müəyyən etmişdir. Bir çox maraqlı tədqiqatlar nəticəsində müəyyən edilmişdir ki, bu sinif birləşmələrin bir çox nümayəndəsi oksid və ya metal örtüklərin alınmasında və bir çox üzvi sintez proseslərində effektiv katalizatorların istehsalı üçün ilkin xammal kimi istifadə edilə bilər.

Açar sözlər: kompleks, analiz, sintez, temperatur, liqand, məhlul.

СИНТЕЗ И ПРИМЕНЕНИЕ КОМПЛЕКСОВ ТРЕХВАЛЕНТНОГО РЕНИЯ (RE(III)) АЦЕТИЛАЦЕТОНАТА С СОЕДИНЕНИЯМИ МЕТАЛ-МЕТАЛЛОВ

Амирли Ф.А.¹, Гулалов О.М.², Кахраманова Ш.И.³, Шихалиев Н.М.⁴, Алиева П.В.⁵

^{1,2} Азербайджанский Государственный Университет Нефти и Промышленности, Баку, Азербайджан

^{3,4,5} Институт катализа и неорганической химии имени академика М.Нагиева, Баку, Азербайджан

¹ fariz.emirov@asoiu.edu.az, <http://orcid.org/0000-0002-9095-2982>

² omar.gulalov@mail.ru, <http://orcid.org/0000-0003-0555-374X>

³ sahnaz.qehremanova@mail.ru, <http://orcid.org/20000-0001-7955-4118>

⁴ nshkh02@bk.ru, <http://orcid.org/0009-0005-2542-2220>

⁵ piraneeliyeva@gmail.com, <http://orcid.org/0009-0006-5763-7311>

РЕЗЮМЕ

Получены биядерные ацетилацетоновые производные трехвалентного рения и детально изучены их физико-химические и термические свойства. Состав и строения соединений определяли химическими, ИК-спектральными и рентгенофазовыми методами. В ходе исследования предложенных структур полученных соединений методом ИК-спектрального анализа установлено, что спектры поглощения ионных комплексов, содержащих протонированные амины, практически идентичны друг другу. Установлено наличие интенсивных полос при 1380 и 1460 см⁻¹, характерных для симметричных и асимметричных деформационных колебаний метильных групп соответственно. Кроме того, в высокочастотной области спектров выявлено наличие широких интенсивных полос с несколькими максимумами, характерных для валентных колебаний протонированных аминов в области 3050-3250 см⁻¹. Термогравиметрическими методами установлено, что они разлагаются при низких температурах и что во всех случаях конечным твердофазным продуктом является металлический рений. В результате многих интересных исследований установлено, что многие представители этого класса соединений могут быть использованы в качестве исходных продуктов для производства эффективных катализаторов при получении оксидных или металлических покрытий и во многих процессах органического синтеза.

Ключевые слова: комплекс, анализ, синтез, температура, лиганд, раствор.