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COMPLEXATION OF MOLIBDENUM(VI) WITH 6,7-DIHYDROXY-4-METHYL-2-PHENYLCHROMENYLIUM AND ITS HALOGEN DERIVATIVES IN SOLUTIONS

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The complexation of molybdenum(VI) with 6,7-dihydroxy-4-methyl-2-phenylchromenilium (MPDOCh) and its chlorine and bromine derivatives containing a halogen atom in 4th position in phenyl ring was studied. The composition of the complexes Mo(VI) : L = 1:2 was established by classical spectrophotometric methods. Based on a combination of spectrophotometric and mass-spectrometric data, complexation way is proposed. It was shown that MoO_2^{2+} cation acts as a complexing agent, and the ligand involved into reaction in the form of an anhydrobase. The analytical characteristics of the resulting complexes were determined, and it was also noted that the halogen derivatives of MPDOCh form more intensely colored and stable complexes with Mo(VI).

Keywords: 6,7-dihydroxy-4-methyl-2-phenylchromenylium; molybdenum(VI); com-plexation; spectrophotometry.

INTRODUCTION. One of the significant problems of chemical analysis is the control of the heavy metals content in objects of various nature. Polyvalent metals are of interest, in particular, molybdenum, which is an important essential trace element that is part of a number of metal enzymes involved in metabolic processes. The most reactive forms of Mo (VI) in acidic medium are molybdenyl cations MoO_2^{2+}, which can form complex compounds mainly with O- and S-containing ligands [1]. The state of analytical chemistry of molybdenum and methods for its determination were considered in [1–3]. Effective methods have been proposed for determining Mo (VI), for example, atomic absorption [4, 5], voltammetric [6, 7], and mass spectrometric [8]. However, these methods are costly and require highly qualified service. Spectrophotometry remains the simplest and most common method for determining molybdenum [9–12]. The possibility of colorimetric determination of Mo (VI) after its micellar extraction concentration in the form of a complex with salicyl fluorone and a cationic surfactant was shown in [13].

As a rule, Mo (VI) interacts with hydroxyl-containing ligands — hydroxybenzenes, trioxyfluorones, and dioxychromenols (DOCh) mainly in an acidic medium [1-3]. The latter are of interest because they form intensely colored and stable complexes with Mo (VI), W (VI), Bi (III), Ga (III), In (III) and some other metal ions [14, 15]. Using DOCh derivatives, sensitive photometric methods for determining Mo (VI) have been developed [15, 16]. In turn, the potential for modifying the reagents of this class has not been fully exhausted. For example, the introduction of halogen atoms promotes a shift in the pH of complexation to a more acidic region and, consequently, an increase in selectivity, and also often leads to an increase in the contrast of the reaction and the sensitivity of the determination.

Based on the foregoing, the aim of this work is to study the complexation of Mo (VI) with halogen derivatives of 6,7-dihydroxy-4-methyl-2-phenylchromenilium in aqueous solutions; establishing the chemistry of their interaction, as well as determining the corresponding chemico-analytical characteristics.

EXPERIMENT AND DISCUSSION OF THE RESULTS.. Derivatives of dihydroxychromenilia: 6,7-dihydroxy -4 – methyl -2- phenylchromenilium (MPDOCh), 6,7-dihydroxy-4-methyl-2-(4-bromophenyl)-chromenilium (4'-Br-MPDOCh), and 6,7-dihydroxy-4-methyl-2- (4-chlorophenyl)-chromenilium (4'-Cl-MPDOCh) perchlorates were synthesized by condensation of equimolar amounts of pyro-gallol A and the corresponding β-dicarbonyl compound in acetic acid medium with the addition of 50% perchloric acid, according to the scheme:

The individuality and purity of the synthesized compounds were confirmed by high performance liquid chromatography. We used an Agilent Technologies 1260 Infunity chromatograph with an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS mass detector (column temperature 35 °C; DOCh concentration in the analyzed solution 1 mg/ml; injection volume 2 μl; column - Zorbax 4.6×100 mm, 3.5 μm; mobile phase - acetonitrile-0.1% aqueous solution of formic acid, 60:40).

Absorption spectra in the range 380–780 nm were recorded on Specord UV VIS and SF-56 spectrophotometers in cuvettes with an absorbing layer thickness of 1, 2, and 3 cm. The acidity of the medium was monitored using an ESL-63-07 glass electrode paired with silver chloride comparison electrode EVL-1M3 on the I-160 ionomer, calibrated according to standard pH buffer solutions.

DOCh working solutions with concentration of $1 \cdot 10^{-2}$ mol/dm^3 were prepared by dissolving an exact weighed reagent in a mixture of ethanol with dimethylformamide (5 vol%). The initial Mo (VI) solution with a concentration of $1 \cdot 10^{-2}$ mol/dm^3 was prepared by dissolving 1.7651 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in hot distilled water, after cooling to 20 °C bringing volume to 1 l and standardized titrimetrically. Solutions with lower concentrations were obtained by diluting the initial one immediately before use. Reagents of qualification not lower than analytical grade were used, the required acidity was created with solutions of sulfuric acid and sodium hydroxide, and with the help of acetic acetate buffer solution.

To optimize the conditions for the complexation reaction, Mo (VI) and DOCh

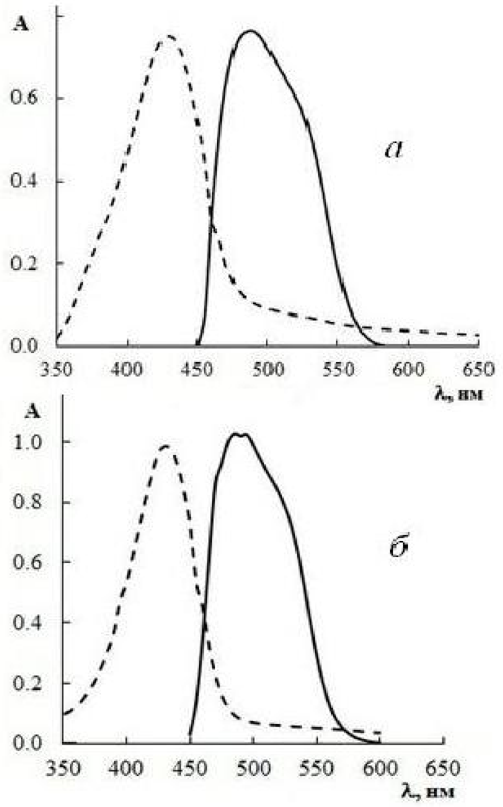


Fig. 1. Light absorption spectra of MPDOCh derivatives (dashed line) and their complexes with Mo (VI): 4'-Cl-MPDOCh (a) and 4'-Br-MPDOCh (b), Mo: L = 1:2, *l* = 1 cm.

solutions with a concentration of $1\cdot10^{-5}$ – $1\cdot10^{-4}$ mol/dm^3 were mixed in different molar ratios in the pH range 1–8 (ΔpH = 0.5) and the light absorption intensity was recorded relative to the solution of the blank experiment. The stoichiometry of the products of interaction was established by the methods of isomolar series, molar ratios, and equilibrium shift; molar absorption coefficients and stability factors were calculated by the method [17]. Mass spectra were recorded by the FAB method on a VG 70-70EQ mass spectrometer using a beam of Xe atoms with an energy of 8 kV.

Changes in the absorption spectra during the complexation of Mo (VI) with different DOChs are similar. Figures 1 and 2 show the absorption spectra in the Mo (VI) –4′-Cl-MPDOCh and Mo (VI)–4′-Br-MPDOCh systems with the ratios Mo : L = 1:2. As seen from fig. 1, the interaction of 4'-Cl-MPDOCh with Mo (VI) is accompanied by a bathochromic shift at 65 nm, 4'-Br-MPDOCh with Mo (VI) – at 70 nm, which indicates an increase in the length of the conjugation chain.

When optimizing the conditions for the interaction of Mo (VI) with MPDOCh derivatives, the influence of the medium acidity was first investigated (Fig. 2). The stoichiometry of complexation was studied under optimal conditions for the interaction of halogen derivatives of DOCh with Mo (VI) using classical methods: isomolar series, metal/ligand saturation, and, as an example, Figure 3 shows the results of processing the ligand saturation curves by the equilibrium shift method. An analysis of these data, as well as those obtained by the methods listed above, allows us to draw a conclusion about the formation of Mo (VI)–DOCh complexes with a composition of 1:2.

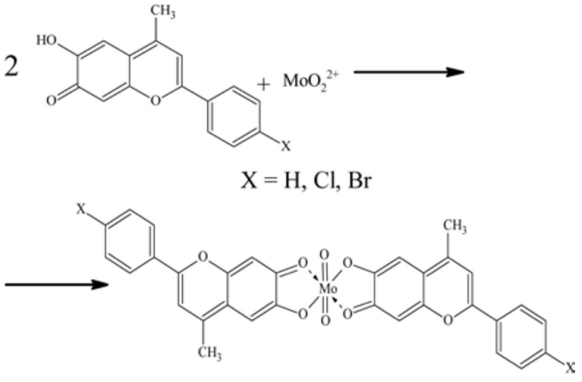
The interaction products in the Mo (VI) – DOCh systems were isolated in a solid state and studied by mass spectrometry with ionization by bombardment with fast atoms (Fig. 4).

In the mass spectrum of the Mo (VI) – PDOCh complexes, a polyisotope cleavage with a maximum at *m/z* 631 is observed, which corresponds to the protonated MoO_2L_2 complex. Signals are present at *m/z* 381 and 395, indicating the cleavage of one MPDOCh molecule and the corresponding MoO_2L^+ particle and the protonated $MoO(OH)_2L$ complex.

A L+ ligand signal with *m/z* 253 and a set of matrix signals are also observed.

In the case of complexes of Mo (VI) with halogen derivatives of MPDOCh, peaks of similar ions are observed in the mass spectra.

Based on the obtained experimental results and published data on the state of Mo (VI) and DOCh in solutions [8, 9], it can be assumed that the complexation scheme has the form of:



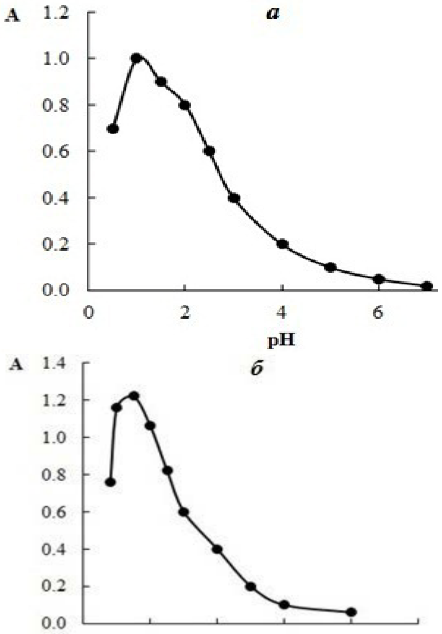


Fig. 2. The effect of pH on the complexation of Mo (VI) with 4'-Cl-MPDOCh (*a*) and 4'-Br-MPDOCh (*b*), *l* = 2 cm.

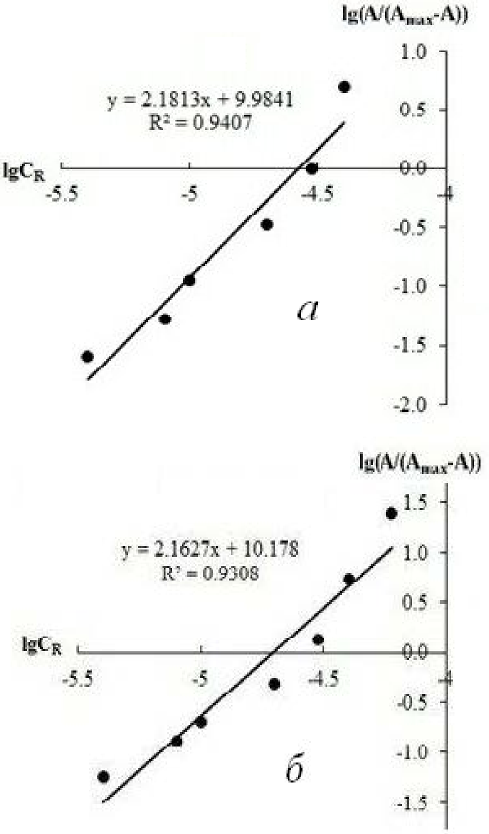


Fig. 3. Determination of the composition of Mo (VI) complexes with 4'-Cl-MPDOCh (*a*) and 4'-Br-MPDOCh (*b*) by the equilibrium shift method. CR = $4\cdot10^{-5}$ M, *l* = 2 cm

The two anhydrobase molecules of the corresponding DOCh form two bonds with the molybdenyl cation through the carbonyl oxygen at position 7 and deprotonated hydroxyl group at position 6. The basic chemical and analytical characteristics of the studied complexes are listed in the table.

According to the table, it can be concluded that the introduction of halogen atoms into the reagent molecule shifts the optimal pH of complexation to the acidic region the stronger, the greater is the electronegativity of the halogen. The molar coefficient of light absorption and the contrast of

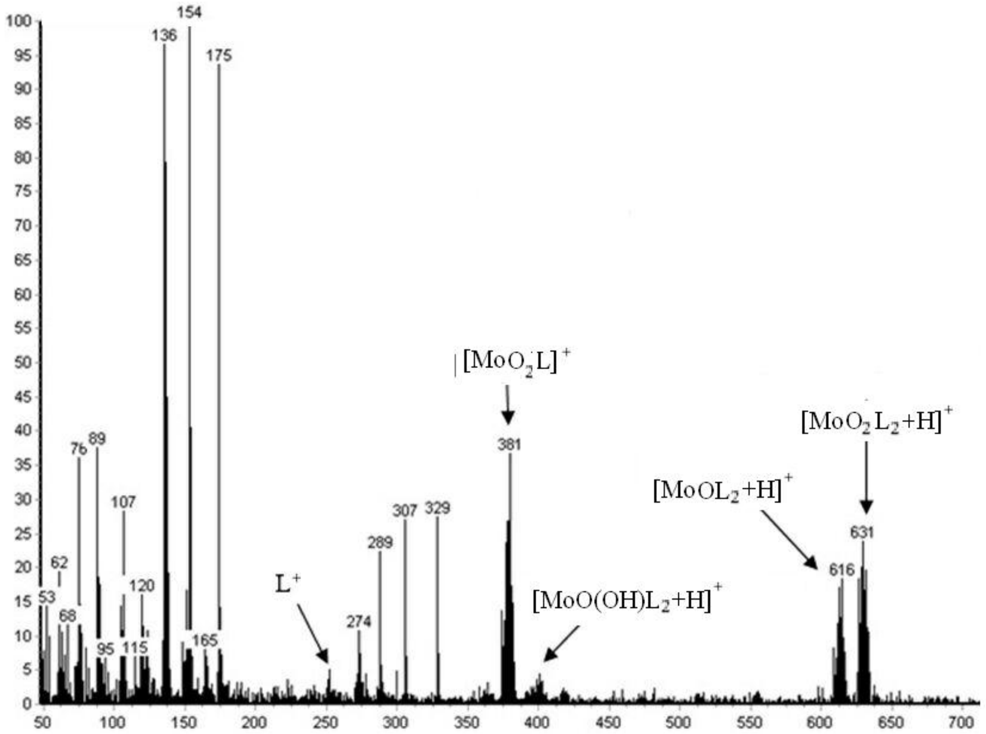


Fig. 4. Mass-spectrum of Mo(VI) complex with MPDOCh

Table

Formation conditions and chemico-analytical characteristics of the Mo(VI) complexes with 6,7-dihydroxy-4-methyl-2-phenylchromenilium derivatives in solutions

Reagent	Mo(VI) : L	pH_{opt}	λ, nm	Δλ, nm	$\varepsilon \cdot 10^{-4}$	lgβ
MPDOCh	1:2	2.5	485	50	1.3	11.23
4'-Br- MPDOCh	1:2	1.5	490	70	2.3	10.18
4'-Cl- MPDOCh	1:2	1.0	495	65	1.9	9.98

the reaction increase in the series MPDOCh - 4'-Cl-MPDOCh - 4'-Br-MPDOCh, which is associated with the effect of “weighting” of the reagent molecule, and the corresponding complexes can be effective analytical forms for the development of methods of photometric and extraction photometric determination of Mo (VI).

CONCLUSIONS. In this work, we determined the chemico-analytical characteristics and composition of the complexes formed in the Mo(VI)–DOCh systems. The composition of the complexes (Mo(VI):DOCh = 1:2) was found by spectrophotometric methods (molar ratios, equilibrium shift). Based on a combination of spectrophotometric and mass spectrometric data, a probable complex chemistry is pro

posed. It was shown that the MoO_2^{2+} cation acts as a complexing agent, and the ligand enters into the reaction in the form of an anhydrobase. It was found that halogen-containing derivatives of MPDOCh form more intensely colored and stable complexes with Mo (VI) than MPDOCh, and the optimal pH of complexation shifts to a more acidic region.

КОМПЛЕКСОУТВОРЕННЯ МОЛІБДЕНУ (VI) З 6,7-ДИГІДРОКСИ-4-МЕТИЛ-2-ФЕНІЛХРОМЕНІЛІЄМ ТА ЙОГО ГАЛОГЕНПОХІДНИМИ В РОЗЧИНАХ

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Досліджено комплексоутворення молібдену(VI) з 6,7-дигідрокси-4-метил-2-фенілхроменілієм (МФДОХ) і його хлор- та бромпохідними, що містять атом галогену в положенні 4 фенільного кільця. Склад комплексів Mo(VI) : L = 1:2 встановлено класичними спектрофотометричними методами. На основі сукупності спектрофотометричних і мас-спектрометричних даних запропоновано хімізм комплексоутворення. Показано, що комплексоутворювачем виступає катіон MoO_2^{2+}, а ліганд вступає в реакцію у формі ангідроснови. Визначені хіміко-аналітичні характеристики утворених комплексів, а також відмічено, що галогенпохідні МФДОХ утворюють більш інтенсивно забарвлені і стійкі комплекси з Mo(VI).

Ключові слова: 6,7-дигідрокси-4-метил-2-фенілхроменілій; молібден(VI); комплексоутворення; спектрофотометрія.

КОМПЛЕКСООБРАЗОВАНИЕ МОЛИБДЕНА (VI) С 6,7-ДИГИДРОКСИ-4-МЕТИЛ-2-ФЕНИЛХРОМЕНИЛИЕМ И ЕГО ГАЛОГЕНПРОИЗВОДНЫХ В РАСТВОРАХ

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Синтезирован ряд галогенсодержащих производных перхлората 6,7- дигидрокси-4-метил-2-фенилбензопирилия. Исследованы особенности комплексообразования молибдена(VI) с 6,7-дигидрокси-4-метил-2-фенилхроменилием и его хлор и бромопроизводными, которые содержат атом галогена в положении 4 фенильного кольца. Состав комплексов Mo(VI):L = 1:2 установлен классическими спектрофотометрическими методами. Определены молярные коэффициенты светопоглощения комплексов молибдена(VI) с незамещенным и хлоро- и бромопроизводными перхлората 6,7-дигидрокси-4-метил-2-фенилхроменилия, которые соответственно составляют $1{,}3\cdot10^4$, $1{,}9\cdot10^4$ и $2{,}3\cdot10^4$. Рассчитано логарифмы констант устойчивости, которые соответственно равны 11,23, 9,98 и 10,18. На основании совокупности спектрофотометрических и масс-спектрометрических данных предложен вероятный механизм комплексообразования молибдена(VI) с производными перхлората 6,7-дигидрокси-4-метил-2-фенилбензопирилия. Показано, что при оптимальных условиях взаимодействия комплексообразователем выступает катион молибденила, а лиганд вступает в реакцию в форме ангидрооснования. Определены химико-аналитические характеристики образованных комплексов, а также отмечено, что галогенпроизводные МФДОХ образуют более интенсивно окрашенные и достаточно устойчивые комплексы с Mo(VI). Отмечено, что молярный коэффициент светопоглощения увеличивается с увеличением молярной массы соответствующих комплексов. Показано, что оптимальное pH комплексообразования сдвигается в кислую область тем сильнее, чем больше электроотрицательность галогена в молекуле лиганда. Отмечено, что новые комплексы молибдена (VI) с хлоро- и бромопроизводными перхлората 6,7-дигидрокси-4-метил-2-фенилхроменилия является электронейтральными и пригодными для разработки экстракционных и сорбционных методик концентрирования микроколичеств молибдена(VI). К тому же, предлагаемые комплексы могут быть использованы в качестве новых аналитических форм для прямого спектрофотометрического определения следовых количеств молибдена(VI) в объектах различной природы.

Ключевые слова: 6,7-дигидрокси-4-метил-2-фенилхроменилий; молибден(VI); комплексообразование; спектрофотометрия.

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