

КОМПЛЕКСЫ ИЗОТИАДИАЗОЛСОДЕЖАЩЕГО БРОМНИТРОЗАМЕЩЕННОГО ТРЕХЗВЕННОГО ПРОДУКТА С D-МЕТАЛЛАМИ (Ni, Co, Zn)**Т.В. Кудаярова, М.А. Тютинна, Е.А. Данилова**

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Настоящая работа является продолжением исследований в области синтеза замещенных макрогетероциклических соединений с 3,5-диамино-1,2,4-тиадиазольными фрагментами. В работе представлены данные по синтезу металлокомплексов на основе изотиадиазолсодержащего бромнитрозамещенного трехзвенного продукта, полученного нами ранее, с двухвалентными d-металлами (Ni, Co, Zn). Взаимодействием 3,5-бис[5(6)-бром-6(5)-нитро-3-иминоизоиндолин-1-илиденамиино]-1,2,4-тиадиазола с ацетатами d-металлов в 2-этоксиэтаноле при температуре 100 °С в течение 2 ч были получены комплексы замещенных трехзвенных продуктов ВАВ-типа с 1,2,4-тиадиазольным фрагментом. По окончании выдержки реакционную массу выливали в воду, выпавший осадок отфильтровывали, промывали 5 % аммиаком, водой, горячими органическими растворителями (ацетоном, метанолом, диметилформамидом, пиридином). Выход целевых продуктов при этом составили 18 -28 %. Полученные металлокомплексы представляют собой порошки темно-коричневого цвета хорошо растворимые в спиртах, ДМФА, не растворимые в воде, гексане и дихлорметане. Строение установлено на основании данных масс-спектрометрии, элементного анализа, электронной, ИК спектроскопии. Синтезированные металлокомплексы трехзвенных продуктов будут в дальнейшем использованы для получения новых представителей замещенных макрогетероциклических соединений различного строения с 3,5-диамино-1,2,4-тиадиазольными фрагментами. Анализ масс-спектров полученных комплексов показал, что по аналогии с литературными данными для трехзвенных продуктов с 2,5-диамино-1,3,4-тиадиазолом, металлокомплексы трехзвенных продуктов с 3,5-диамино-1,2,4-тиадиазолом были выделены в виде аквакомплексов. Это подтвердилось данными атомно-абсорбционного анализа, где наблюдается удовлетворительная сходимость экспериментальных и вычисленных значений, что подтверждает строение аквакомплексов состава 1:1.

Ключевые слова: синтез, металлокомплексы, изотиадиазолсодержащий бромнитрозамещенный трехзвенный продукт, свойства

COMPLEXES OF IZOTHIADIAZOLE-CONTAINING BROMONITROSUBSTITUTED THREE UNITS PRODUCT WITH D-METALS (NI, CO, ZN)

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This work is continuation of synthesis researches of substituted macroheterocyclic compounds with 1,2,4-thiadiazole fragments. Data of synthesis of complexes with divalent d-metals (Ni, Co, Zn) on the basis of received earlier brominenitrosubstituted isothiadiazole three-unit product are presented. Complexes of BAB-type product consisting 1,2,4-thiadiazole and bromine-nitro-isoindole fragments were received by interaction 3,5-bis-[5(6)-bromine-6(5)-nitro-3-iminoisoindolin-1-ilidenamiino]-1,2,4-thiadiazol with acetates of d-metals in 2-ethoxyethanol at 100 °C for 2 h. After the reaction the mixture was poured into water and precipitate was filtered and washed with 5 % ammonia, water and hot organic solvents (acetone, methanol, dimethylformamide, pyridine). Yield of target products was 18 – 28 %. The resulting complexes are dark brown powders with high solubility in alcohols, DMF, insoluble in water, dichloromethane and hexane. The structures of products were established by data of mass spectrometry, elemental analysis, UV-vis and IR spectroscopy. Data of MALDI-TOF mass spectrometry showed that complexes with metal of three-unit product with 1,2,4-thiadiazole fragment were isolated as monohydrate by analogy with literary for 1,3,4-thiadiazole. Data of atomic absorption analysis with good convergence of the experimental and calculated values confirmed monohydrate structure these products. These complexes of three-unit products will be used for synthesis of new various substituted macroheterocycles with 1,2,4-thiadiazole fragments.

Key words: synthesis, metal complexes, izothiadiaazole-containing bromonitrosubstituted three units product, properties

Для цитирования:

Кудаярова Т.В., Тютина М.А., Данилова Е.А. Комплексы изотиадиазолсодержащего бромнитрозамещенного трехзвенного продукта с d-металлами (Ni, Co, Zn). *Изв. Вузов. Химия и хим. технология*. 2018. Т. 61. Вып. 12. С. 68–73

For citation:

Kudayarova T.V., Tyutina M.A., Danilova E.A. Complexes of izothiadiaazole-containing bromonitrosubstituted three units product with d-metals (Ni, Co, Zn). *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2018. V. 61. N 12. P. 68–73

INTRODUCTION

This work is continuation of research in the field of synthesis of substituted ABAB- and ABBB-types macroheterocyclic compounds (A – 1,2,4-thiadiazole, B – isoindole fragments) [1-4].

Previously by the interaction of 3,5-diamino-1,2,4-thiadiazole **1** with the corresponding substituted phthalonitriles or 1,3-diiminoisoindolines we synthesized three-unit products (TUPs) of BAB-type. Structures of BAB-type products were established on the basis of IR, UV spectroscopy and elemental analysis data [5]. Three-unit products contain reaction centers capable of interacting with ions of various metals with the formation of complex compounds [6, 7]. It is known that three-unit intermediates are thermally unstable, therefore, their metal complexes are more preferable to production of Mc ABBB-type [9-14]. Most often, nickel Ni²⁺ – a metal with a smaller ionic radius,

which in size more corresponds to the coordination cavity of the ligand [15], is used as a complexing agent from a number of divalent d-elements.

Therefore, the present work is devoted to the synthesis of complexes of isothiadiazole-containing bromonitrosubstituted TUP [5] with divalent d-metals, in order to obtain on their basis noncentrosymmetric complexes of macro-heterocyclic compounds of the ABBB type.

EXPERIMENTAL

The electronic absorption spectra of synthesized compounds in the visible and UV regions were recorded on a HITACHI U-2001 spectrophotometer at room temperature, in the range of 250-800 nm in quartz rectangular cuvettes 1-10 mm.

IR spectra were recorded on an AVATAR 360 FT-IR spectrometer. Samples for IR spectra in the form of tablets were prepared by thoroughly rub-

bing the sample in KBr and pressing, or dissolving in an organic solvent and applying the solution on the on the red glass, with further evaporation of the solvent.

The metal content (mass concentration of the element, mg/l) in the corresponding metal complexes for the solution obtained from the decomposition of this complex in nitric acid (HNO₃ HF) was determined by atomic absorption analysis using a Buck VGP210 spectrometer.

MALDI-TOF mass spectra were obtained using the AXIMA Confidence mass spectrometer (SHIMADZU) in the positive ion mode using DHB (2,5-dihydroxybenzoic acid), CHCA (α -cyano-4-hydroxycinnamic acid) as the matrix.

3,5-Bis[5(6)-bromo-6(5)-nitro-3-iminoisoindolin-1-ylidenemino]-1,2,4-thiadiazole 1 was prepared according to the procedure of [5].

General method: mixture of 0.5 mmol three-unit product **1**, 0.5 mmol acetate of metal and 5 ml of 2-ethoxyethanol was stirred at 100 °C for 2 h. After cooling to r.t., reaction mixture was poured into water, the precipitate formed was filtered off, washed with 5 % ammonia, water, hexane, dichloromethane and methanol. The product was dried at 100 °C for 4 h.

Aqua[3,5-bis(5(6)-brom-6(5)-nitro-3-iminoisoindoline--1-ylidenamino)-1,2,4-thiadiazole]nickel (II) (2): was prepared according to general methodic by interacting 0.34 g **1** and 0.124 g Ni(OAc)₂·4H₂O. Yield: 0.096 g (26%). UV-vis (DMF), λ_{\max} (lg ϵ , mol⁻¹·L·cm⁻¹), $c = 1.12 \cdot 10^{-4}$ M, nm: 365 (3.48). IR (KBr), $\bar{\nu}/\text{cm}^{-1}$: 3383, 1587 (NO₂ asym.), 1467, 1343 (NO₂ sym.), 1178, 909, 746. 621, 556 (C-Br). Found, %: Ni 8.04. Calcd. to C₁₈H₈Br₂N₁₀NiO₄S·H₂O, %: Ni 8.42. MALDI-TOF, m/z: 679 [M + 3H]⁺, 691[M + O]⁺. EM 675.82.

Aqua[3,5-bis(5(6)-bromo-6(5)-nitro-3-iminoisoindoline--1-ylidenamino)-1,2,4-thiadiazole]cobalt(II) (3): was synthesized according to general procedure by interacting of 0.34 g **1**, 0.125 g

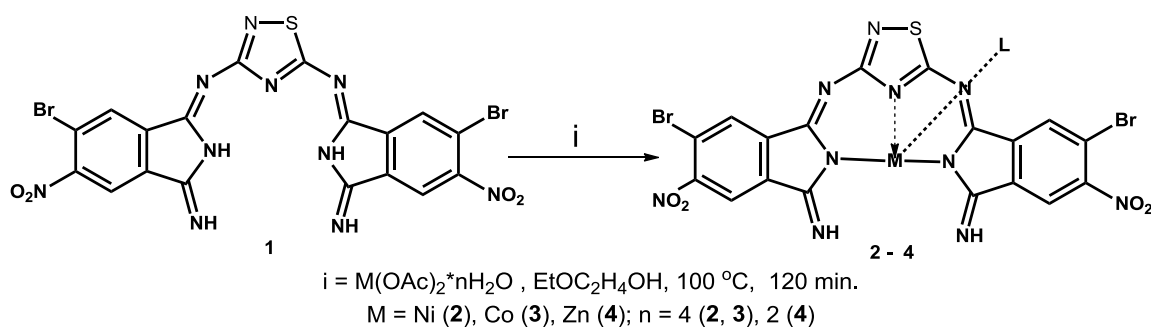
(0.5 mmol) Co(OAc)₂·4H₂O. Yield: 0.105 g (28.3%). UV-vis (DMF), λ_{\max} (lg ϵ , mol⁻¹·L·cm⁻¹), $c = 1.22 \cdot 10^{-4}$ M, nm: 374 (3.7). IR (KBr), $\bar{\nu}/\text{cm}^{-1}$: 3419, 1733, 1616, 1537(NO₂ asym.), 1463, 1377 (NO₂ sym.), 1156, 1077, 865, 733, 536 (C-Br). Found, %: Co 8.21. Calcd. to C₁₈H₈Br₂N₁₀CoO₄S₁·H₂O, %: Co 8.45. MALDI-TOF, m/z: 714[M+2H₂O]⁺, 687 [M-NO₂+K+O]⁺, 547 [M-2NO₂-Br+K]⁺. EM 676.8.

Aqua[3,5-bis(5(6)-bromo-6(5)-nitro-3-iminoisoindoline--1-ylidenamino)-1,2,4-thiadiazole]zinc(II) (4): was prepared according to general procedure by interaction of 0.34 g **1**, 0.11 g Zn(OAc)₂·2H₂O. Yield: 0.066 g (17.7 %). UV-vis (DMF), λ_{\max} (lg ϵ , mol⁻¹·L·cm⁻¹), $c = 1.18 \cdot 10^{-4}$ M, nm: 362 (3.81). IR (KBr), $\bar{\nu}/\text{cm}^{-1}$: 3438, 1726, 1635, 1539 (NO₂ asym.), 1457, 1391 (NO₂ sym.), 1086, 855, 653, 562 (C-Br). Find, %: Zn 8.98. Calcd. for C₁₈H₈Br₂N₁₀ZnO₄S₁·H₂O, %: Zn 9.29. MALDI-TOF (DHB), m/z: 720 [M + K]⁺, 650 [M-NO₂+O]⁺, 622 [M-Br +H₂O+2H]⁺, 608 [M-2NO₂+H₂O]⁺, 596 [M-2NO₂+Li]⁺. EM 681.8.

DISCUSSION

The authors of [15] using semiempirical quantum chemical methods studied the electronic and spatial structure of the TUP and found that they are structurally non-rigid compounds with pronounced propensity to rotational isomerism, plane inversion, and tautomeric transformations. Therefore, introduction divalent metal into the molecular center of the molecule stabilize the *cis*-form of the TUP.

The preparation of complexes **2-4** was carried out by reacting 3,5-bis[5(6)-bromo-6(5)-nitro-3-iminoisoindoline-1-ylidenamino]-1,2,4-thiadiazole **1** with acetates of Ni, Co, Zn, respectively, in 2-ethoxyethanol (*Scheme 1*).



Scheme 1. The synthesis of complexes of izothiadiaazole-containing bromonitrozsubstituted three units product with d-metals (Ni, Co, Zn)
Схема 1. Синтез комплексов изотиadiaзолсодержащего бромнитрозамещенного трехзвенного продукта с d-металлами (Ni, Co, Zn)

After the end of aging, the reaction mass was poured into water, the precipitate formed was filtered off, washed with 5% ammonia, water and hot organic solvents (acetone, methanol, dimethylformamide, pyridine). The yield of the target products was 18-28%.

Complexes **2-4** are dark brown powders with high solubility in alcohols, DMF. The absence of solubility in water, hexane, and dichloromethane allowed using these solvents for purification from a three-link product.

The structure of the compounds is established on the UV-vis, IR spectroscopy, mass spectrometry, and elemental analysis data.

Changes in both the UV and the IR spectra are evidence of the entry of metal into the coordination cavity of compounds **2-4**.

Thus, a slight hypsochromic shift of the absorption band occurs at the transition from the three-unit ligand to the nickel complex **2** and one intense absorption maximum is observed at 365 nm in the electronic absorption spectrum.

Absorption bands at 1615 cm^{-1} by deformation vibrations of N-H bonds of cyclic imino groups for **1** are not found for **2-4**, which confirms the entry of the metal in the IR spectra of complexes. At the same time, the absorption bands of asymmetric (1571 cm^{-1}) and symmetric (1343 cm^{-1}) stretching vibrations of NO_2 -group bonds and the band of stretching vibrations of the C-Br bond at 568 cm^{-1} are preserved [16].

Peaks corresponding to the complex of a three-unit product with one metal atom with $m/z = 679$ $[\text{M}+3\text{H}]^+$ are observed in the mass spectrum of **2** (Fig. 1). The isotopic distributions of the signals of the obtained complex completely coincides with the theoretically calculated.

In addition, peak with $m/z = 691$ corresponds to the structure of $[\text{M}+\text{O}]^+$ in the mass spectrum. The presence of atomic oxygen in the TUP structure corresponds to the results obtained for the hemihexaphyrazine complex with Cu(II) [17]. This explains by the fact that a solid sample undergoes a powerful energy action-laser radiation in the mass spectrometry. As a result, extraligands are split off and the already changed complex passes into the gaseous phase [17-18].

The stability of the molecular ion can decrease due to the presence of nitrogen-containing substituent's ($-\text{NO}_2$, $\text{O}-\text{N}=\text{O}$, $-\text{O}-\text{NO}_2$) and halogens (Cl, Br, I) [19]. Moreover, the loss of the oxygen atom for all types of nitrocompounds and the NO molecule is characteristic, which was discovered in the mass-spectral analysis of synthesized products 3-4.

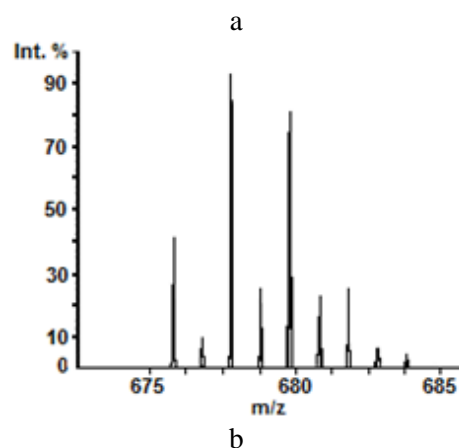
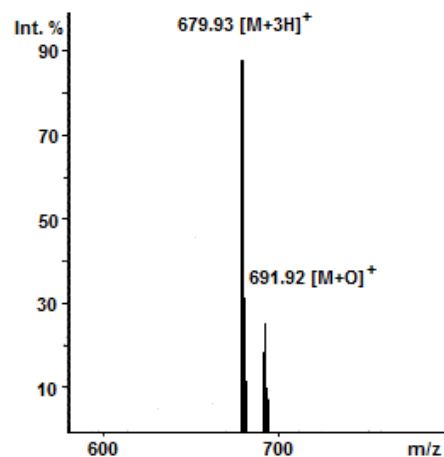


Fig. 1. MALDI-TOF mass spectrum of complex **2**: experimental (a) and isotopic distribution (b)

Рис. 1 MALDI-TOF масс-спектр комплекса **2**: экспериментальный (a) и изотопное распределение (b)

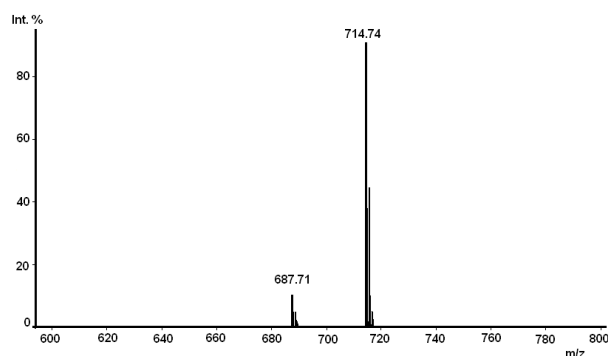


Fig. 2. MALDI-TOF mass spectrum of complex **3**

Рис. 2 MALDI-TOF масс-спектр комплекса **3**

Thus, peak with $m/z = 714$ $[\text{M}+2\text{H}_2\text{O}]^+$ and peaks of fragmentation products with $m/z = 687$ $[\text{M}-\text{NO}_2+\text{K}+\text{O}]^+$ and $m/z = 547$ $[\text{M}-2\text{NO}_2-\text{Br}+\text{K}]^+$ in the mass spectrum of complex with cobalt **3** (Fig. 2) were discovered.

Molecular ions of target compound and the fragmentation products for the complex with zinc **4** have also been detected.

Analysis of the mass spectra of the complexes **2-4** showed aquacomplexes with metal of TUP with

3,5-diamino-1,2,4-thiadiazole like by TUP with 2,5-diamino-1,3,4-thiadiazole [20]. The structure of aqua complexes of composition 1: 1 was confirmed by the data of atomic absorption analysis with satisfactory convergence of the experimental and calculated values.

CONCLUSIONS

The interaction by 3,5-bis[5(6)-bromo-6(5)-nitro-3-iminoisoindoline-1-ylidenamino]-1,2,4-thiadiazole with acetates of *d*-metal in 2-ethoxyethanol gave complexes of substituted three-unit products of

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BAB-type. The structure is established on mass spectrometry, elemental analysis, UV-vis and IR spectroscopy data. The resulting metal complexes of three-unit products will use in the synthesis of macroheterocyclic compounds of various structures.

ACKNOWLEDGEMENTS

The research was performed using resources of the Center for Collective Use, Ivanovo State University of Chemical Technology "ISUCT".

The work was performed under the State contract (Project part), project No. 4.3232.2017/4.6.

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Поступила в редакцию 09.04.2018
Принята к опубликованию 22.10.2018

Received 09.04.2018
Accepted 22.10.2018