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### SYNTHESIS AND OPTICAL PROPERTIES OF FERROCENE COMPLEX COMPOUNDS WITH SOME 3D METALS BASED ON $\beta$ -DICARBONYL DERIVATIVES

Abstract

We obtained  $\beta$ -diketone, 1-ferrocenylbutanedione-1,3, by Claisen condensation. Ligands - hydrazones of monocarboxylic acids 1-ferrocenylbutanedione-1,3 ( $H_2L$ ) were synthesized by the interaction of carboxylic acid hydrazides with ferrocenylacetone. The optical properties of all compounds synthesized in the work have been studied; based on the absorption spectra data, the values of the optical band gap were determined; it was shown that all the synthesized compounds are  $d-\pi$  type chromophores and have a band gap of 1.39-2.26 eV, i.e. they belong to narrow-gap semiconductors.

**Keywords:** monoacetylferrocene, hydrazone, Claisen ester condensation, electronic spectra, chromophores, band gap.

### СИНТЕЗ И ОПТИЧЕСКИЕ СВОЙСТВА КОМПЛЕКСНЫХ СОЕДИНЕНИЙ ФЕРРОЦЕНА С НЕКОТОРЫМИ 3D-МЕТАЛЛАМИ НА ОСНОВЕ $\beta$ -ДИКАРБОНИЛЬНЫХ ПРОИЗВОДНЫХ

Аннотация

Нами конденсацией Кляйзена получен  $\beta$ -дикетон – 1-ферроценилбутандион-1,3. Синтезированы лиганды - гидразоны монокарбоновых кислот 1-ферроценилбутандиона-1,3 ( $H_2L$ ) взаимодействием гидразидов карбоновых кислот с ферроценилацетоном. Исследованы оптические свойства всех синтезированных в работе соединений; на основе данных спектров поглощения определены значения оптической ширины запрещенной зоны; показано, что все синтезированные соединения являются хромофорами типа  $d-\pi$  и обладают шириной запрещенной зоны 1,39-2,26 эВ, то есть относятся к узкозонным полупроводникам.

**Ключевые слова:** моноацетилферроцен, гидразон, сложноэфирная конденсация Кляйзена, электронные спектры, хромофоры, запрещенная зона

### FERROTSENNING $\beta$ -DIKARBONIL HOSILALARI ASOSIDA BA'ZI BIR 3D METALLAR BILAN KOMPLEKS BIRIKMALAR SINTEZI VA OPTIK XOSSALARI

Annotasiya

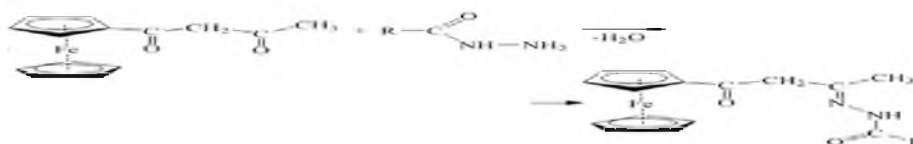
Klyayzen kondensasiyasi orqali  $\beta$ -diketon – 1-ferro-senilbutandion-1,3 olindi. Monokarbon kislota gidrazidlari va ferrosenoilasetonning o'zaro ta'sirlashuvi natijasida ligandlar – gidrazonlar ( $H_2L$ ) sintez qilindi. Ishda sintez qilingan barcha birikmalarning optik xossalari o'rganildi; yutilish spektrlari ma'lumotlari asosida optik ta'qiqlangan sohaning qiymatlari aniqlandi; barcha sintez qilingan birikmalar  $d-\pi$  tipidagi xromoforlar bo'lib, ta'qiqlangan soha kengligi 1,39-2,26 eV ekanligi, ya'ni tor sohada yarim o'tkazgich xossaga ega ekanligi aniqlandi.

**Kalit so'zlar:** monoasetilferrosen, gidrazon, Klyayzenning murakkab efir kondensasiyasi, elektron spektrlar, xromoforlar, ta'qiqlangan soha

**Introduction:** Ferrocene chemistry continues to develop rapidly throughout the world. Wide area application of derivatives of ferrocene depends on their properties.

**Literature review:** Of great importance is the production of ferrocene derivatives of chemo- and biosensors, redox-active DNA markers, redox labels, "smart glasses", "smart watches", structural materials for magnetic and random access memory, materials with liquid crystal properties, turnstiles, molecular magnets, solar batteries, in medicine: anti-cancer, antimicrobial and anti-anemic agents, electrochemical glucometers, liquid-crystal indicators, etc. At present, ferrocene-containing complex compounds are often included in the composition of materials used in photonics and nonlinear optics, they are used as ligands in the creation of chemosensors, are being investigated as molecular tweezers, rotors, shuttles, brakes, turnstiles, etc. [1, 2, 3].

**Research Methodology:** Interaction of alcohol solutions of equimolar amounts 1-ferrocenylbutanedione-1,3 with alcohol solutions of acetylhydrazide, benzoylhydrazide, meta- and para-nitrobenzoylhydrazides, hydrazides of 5-bromosalicylic and phenylacetic acids, thiosemicarbazide, new ligands  $H_2L^1 - H_2L^7$  were synthesized, respectively [4, 5, 6, 7, 8, 9,10].



X=O: R=CH<sub>3</sub> (H<sub>2</sub>L<sup>1</sup>), C<sub>6</sub>H<sub>5</sub> (H<sub>2</sub>L<sup>2</sup>), *m*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub> (H<sub>2</sub>L<sup>3</sup>), *n*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub> (H<sub>2</sub>L<sup>4</sup>), 2-OH-5-Br-C<sub>6</sub>H<sub>3</sub> (H<sub>2</sub>L<sup>5</sup>), C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> (H<sub>2</sub>L<sup>6</sup>). X=S, R=NH<sub>2</sub>, (H<sub>2</sub>L<sup>7</sup>).

**Analysis and results.** To reveal the optical properties of the synthesized compounds, we recorded the electronic absorption spectra for all derivatives of ferrocene obtained in the work in ethanol. The positions of the absorption maxima were determined from the electronic absorption spectra ( $\lambda^{\text{abs}}_{\text{max}}$ ) and the value of the start of absorption ( $\lambda^{\text{abs}}_{\text{onset}}$ ), as well as the value of the molar extinction coefficient ( $\epsilon$ ) and calculated on the basis of the beginning of the absorption of the value of the band gap (Table 1). Figure 1 shows the absorption spectra of monoacetylferrocene, ferrocenoylacetone, and ferrocenoylferrocene ligands H<sub>2</sub>L<sup>2</sup> and H<sub>2</sub>L<sup>3</sup>. In the spectrum of ligands, the long-wavelength maximum in the region 417-485 nm is associated with intramolecular charge transfer and corresponds to  $\pi$ - $\pi^*$  transitions occurring in the cyclopentadienyl part of the molecules. In the spectrum of monoacetylferrocene (MAF), the short-wavelength maximum at 256 nm changes in ferrocenoylacetone (FA), absorption maxima at 450 ( $\epsilon=2.94$ ) and 536 ( $\epsilon=3.21$ ) nm show hypochromic [417 nm ( $\epsilon=1.79$ ) and 459 nm ( $\epsilon=1.91$ )]. In the spectrum of ligands H<sub>2</sub>L<sup>1</sup>- H<sub>2</sub>L<sup>7</sup>, the long-wavelength absorption maximum in the region of 310-536 nm disappears. In the absorption spectrum of the H<sub>2</sub>L<sup>5</sup> ligand, which contains the OH and Br auxochromes, the expected increase in the intensity of semiconductors, for which the band gap is less than or equal to 2,18, is expected. The introduction of substituents into the benzene nucleus causes a bathochromic or hypsochromic shift of the corresponding absorption bands, together with a hyperchromic effect. Short-wavelength absorption maxima in the spectra of the ligands H<sub>2</sub>L<sup>2</sup> (benzoylhydrazone of ferrocenoylacetone), H<sub>2</sub>L<sup>3</sup> nitrobenzoylhydrazone of ferrocenoylacetone) and H<sub>2</sub>L<sup>5</sup> (hydrazone 5-bromosalicylic acid) appear at 243, 228, 329, 340 and 486 nm respectively. In the absorption spectrum of the H<sub>2</sub>L<sup>2</sup> and H<sub>2</sub>L<sup>5</sup> ligands, the bathochromic shift of the benzene band is associated with  $\pi$ - $\pi^*$  transitions in the benzene chromophore [11, 12, 13, 14, 15].

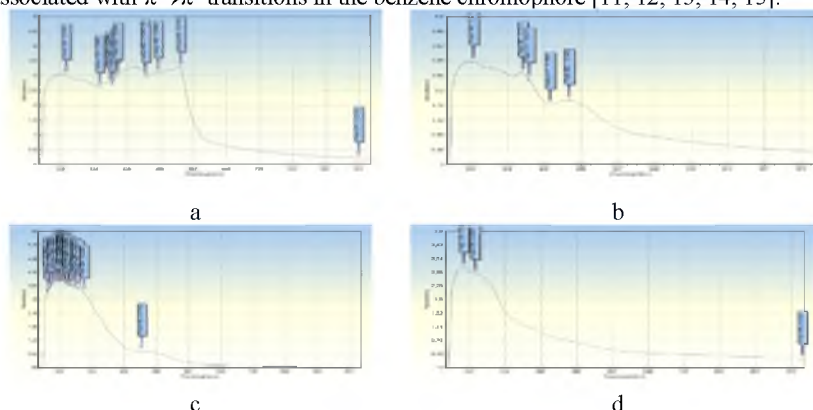


Fig. 1. EAS: MAF (a), FA (b), H<sub>2</sub>L<sup>6</sup> (c) and H<sub>2</sub>L<sup>7</sup> (d) in ethanol.

Table 1  
Obtained and calculated optical characteristics of MAF, FA and ligands based on the data of electronic absorption spectra (solvent-absolute ethanol, concentration 10<sup>-5</sup> M)

Compound	$\lambda^{\text{abs}}_{\text{max}}$ , nm	$\lambda^{\text{abs}}_{\text{onset}}$ , nm	$E_g^{\text{opt}}$ , eV	$\epsilon$ , l·mol <sup>-1</sup> ·cm <sup>-1</sup>
MAF	256, 369, 450, 480, 536	729	1,7	3,016; 2,65; 2,94; 3,1; 3,27
FA	248, 357, 372, 417, 459	891	1,39	3,06; 2,72; 2,55; 1,798; 1,92
H <sub>2</sub> L <sup>1</sup>	220, 341	650	1,91	2,88; 2,77
H <sub>2</sub> L <sup>2</sup>	230, 243, 304, 449	650	1,91	3,767; 3,92; 3,3036; 0,7443
H <sub>2</sub> L <sup>3</sup>	230, 255	730	1,7	2,808; 2,6162
H <sub>2</sub> L <sup>4</sup>	230, 304, 449	650	1,91	3,767; 3,3036; 0,7443
H <sub>2</sub> L <sup>5</sup>	243, 228, 329, 340, 486	648	1,92	3,4248; 3,3316; 2,8582; 0,7441
H <sub>2</sub> L <sup>6</sup>	215, 324	646	1,91	3,31; 3,30
H <sub>2</sub> L <sup>7</sup>	220, 328	656	1,89	3,314 3,302
$E_g^{\text{opt}} = 1240/\lambda^{\text{abs}}_{\text{onset}}$				

**Conclusion.** The compounds synthesized in the work are chromophores of the type d- $\pi$ . Among the obtained ligands, H<sub>2</sub>L<sup>2</sup> has a high long-wavelength absorption maximum ( $\lambda^{\text{abs}}_{\text{max}}=449$  nm), while the H<sub>2</sub>L<sup>3</sup> ligand has the highest value of the long-wavelength onset of intrinsic absorption ( $\lambda^{\text{abs}}_{\text{onset}} = 730$ ), as a result, the band gap of this ligand has the smallest value among the ligands synthesized by us and is 1.7 eV.

Based on the EAS results, it is determined that the width of the optically forbidden band is in the range of 1.39-2.26 eV and they belong to the class narrow-gap semiconductors (chromophores of the d- $\pi$  type).

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