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SYNTHESIS OF DEHYDROACETIC ACID DERIVATIVES WITH CHROMOPHORIC CHAINS AND THEIR COMPLEXES WITH ZIRCONIUM PHTHALOCYANINE *

Dyes based on derivatives of dehydroacetic acid were synthesized by its condensation with aldehydes. The synthesized compounds were used to prepare out-of-plane complexes with zirconium phthalocyanine. The composition, structure and spectral properties of the compounds were characterized by NMR and UV-Vis spectroscopy. An additional chromophore in the macrocyclic system is manifested by the broadening of the Soret band, its bathochromic shift and appearance of shoulder on the red side of the Soret band.

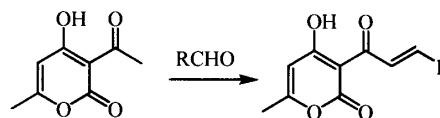
Keywords: dehydroacetic acid, zirconium phthalocyanine, UV-Vis spectroscopy.

INTRODUCTION. Phthalocyanines are widely studied as photosensitizers to create artificial photosynthetic systems for the conversion of solar energy [1]. Their absorption spectra have two maxima in the visible region: the Soret band (330–340 nm) and the *Q*-band (680–690 nm) [2]. The idea of this work is the synthesis of new phthalocyanine complexes, which have a higher absorption in the visible region. For this purpose, β -diketone ligands, that containing unsaturated chromophoric chain, were introduced into phthalocyanine complexes of zirconium.

Previously, the method of phthalocyanines modification by ligand exchange reaction at the central metal atom of macrocycle have been developed in our group. β -diketones [3], keto-esters [4], dehydroacetic acid (dha) [5] and other compounds with chelating groups in the heterocyclic part of the molecule were successfully used as out-of-plane ligands. The present work describes synthesis of dha derivatives by condensation of dha with aldehydes. The proposed methods is similar to the one given in the work [6].

The presence of several reaction centers in the molecule of dha makes it possible to obtain a wide range of derivatives, including chalcones, condensed and heterocyclic systems such as pyrone, pyrimidine, pyridazine, etc. [7]. These derivatives are used as probes to determine amine in solution [8], antimicrobial or fungicidal agents [7]. The acetyl group of dha quite easily reacts with benzaldehyde in the Claisen–Schmidt reaction. For the first time condensation of

dha with benzaldehyde was described by W.Hale [6]. The structure of the obtained compounds has been clarified and ultimately proved in the work [9]. Thus, it was found that chalcones, which formed by the interaction of dha and aldehydes, are the β -keto-enol heterocyclic systems with chelating groups and unsaturated chain:



Scheme 1.

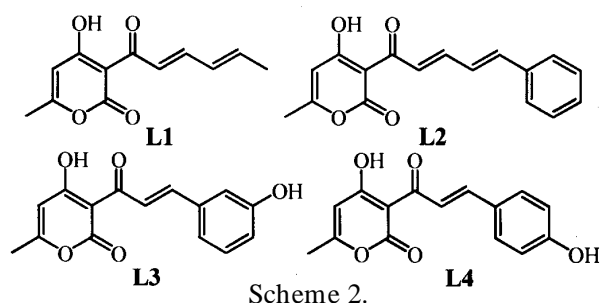
These colored compounds have an absorption maximum in the spectral region between 300 and 450 nm. They are similar to the dha and can form complexes with boron [8, 10] and metals [11–15].

EXPERIMENT AND DISCUSSION. Recently we have reported that the dha forms complexes not only with metal cations, but also with more complex systems, such as coordinatively unsaturated zirconium and hafnium phthalocyanines [5]. The aim of this work was the synthesis and study of the spectral properties of the phthalocyanine complexes of zirconium with dha derivatives as out-of-plane ligands.

Dha derivatives were obtained by condensation reaction with various aldehydes which have unsaturated chain or donor substituents.

Four compounds have been received (scheme 2) with crotonic (L1), cinnamon (L2), and 3- and 4-hydroxybenzaldehydes (L3, L4). All of these substan-

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Scheme 2.

ces possess the yellow-orange color. The absorption maxima of L2 and L4 in UV-Vis spectra are bathochromic shifted to about 30 nm relatively to L1 and L3, respectively (table).

UV-Vis spectroscopy data of the dha derivatives L1–L4 ($C=1 \cdot 10^{-4}$ M) and complexes $PcZr(L1–L4)_2$ ($C=5 \cdot 10^{-5}$ M) in DMSO (λ_{max} , nm, (lg ϵ))

L (free L band)	$PcZrL_2$		
	B-band	band L	Q-band
L1 350 (4.24)	340 (4.56)	—	690 (4.75)
L2 379 (4.29)	346 (4.53)	417 (4.21)	690 (4.75)
L3 366 (4.23)	345 (4.54)	410 (3.60)	690 (4.74)
L4 395 (4.25)	348 (4.54)	413 (4.05)	689 (4.75)

The general method of synthesis of dha condensed derivatives L1–L4. The reactions were performed by slightly modified procedure given in the work [9]. To 0.1 mol of dha in 70 ml of isopropanol was added an equimolar amount of aldehyde and heated up to boiling temperature. 10 drops of a mixture of pyridine and piperidine were added to the boiling homogeneous solution (1:1 by volume) and boiled for 4 h. The half of the solvent was distilled, cooled down and filtered from fell out crystals. The product was washed twice on the filter with small amount of isopropanol and recrystallized from DMF-isopropanol system. After that the product was filtered, washed on the filter with isopropanol, twice with water and air dried.

(L1). 3-(2E,4E)-hexa-2,4-dienoyl-4-hydroxy-6-methyl-2H-pyran-2-one. Yield: 27 %. M.p. = 150–154 °C. Found, %: C 65.53; H 5.41. Anal. Calcd. (%) for $C_{12}H_{12}O_4$: C 65.45; H 5.49. 1H NMR (400 MHz, $CDCl_3$) δ 18.08 (s, 1H), 7.59 (p, $J=15.0$ Hz, 2H), 6.62–6.15 (m, 2H), 5.92 (s, 1H), 2.26 (s, 3H), 1.92 (d, $J=6.0$ Hz, 3H).

(L2). 4-hydroxy-6-methyl-3-((2E,4E) -5-phenylpenta-2,4-dienoyl) -2H-pyran-2-one. Yield: 72 %. M.p. = 170–175 °C. Found, %: C 71.79; H 4.98. Anal. Calcd. (%) for $C_{17}H_{14}O_4$: C 72.33; H 5.00. NMR (400 MHz, $CDCl_3$) δ 18.09 (s, 1H), 7.80 (dt, $J=14.9$, 12.3 Hz, 2H), 7.52 (dd, $J=8.2$, 1.3 Hz, 2H), 7.44–7.31 (m, 3H), 7.18–7.01 (m, 2H), 5.95 (s, 1H), 2.28 (s, 3H).

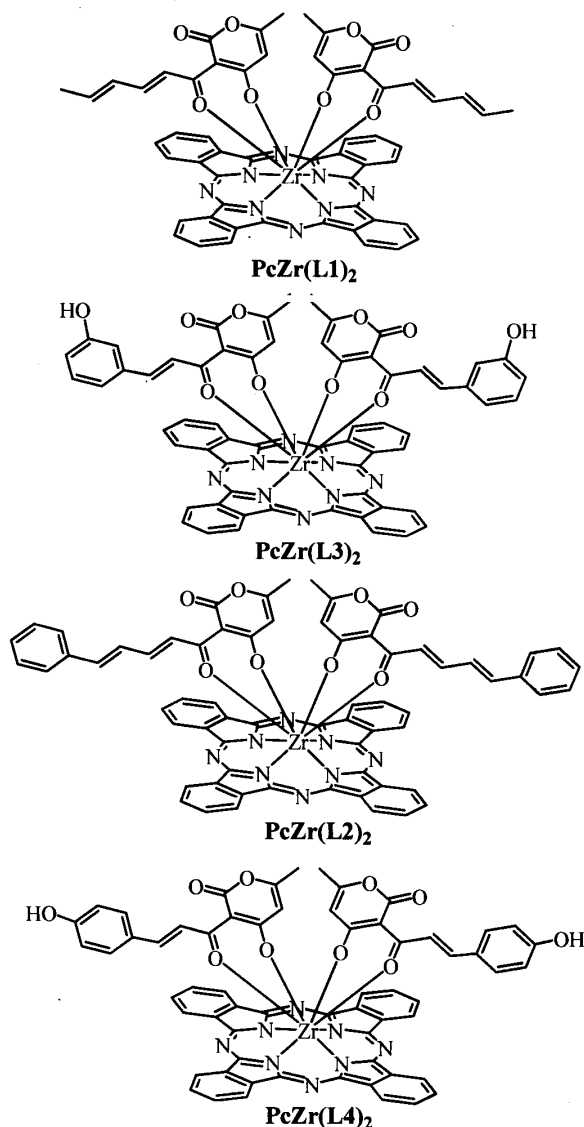
(L3). (E)-4-hydroxy-3-(3-(3-hydroxyphenyl)acryloyl)-6-methyl-2H-pyran-2-one. Yield: 39 %. M.p. = 265–270 °C. Found, %: C 66.13; H 4.51. Anal. Calcd. (%) for $C_{15}H_{12}O_5$: C 66.17; H 4.44. 1H NMR (400 MHz, DMSO) δ 17.66 (s, 1H), 9.77 (s, 1H), 8.11 (d, $J=15.8$ Hz, 1H), 7.81 (d, $J=15.8$ Hz, 1H), 7.28 (t, $J=8.0$ Hz, 1H), 7.13 (d, $J=6.4$ Hz, 2H), 6.89 (dd, 1H), 6.28 (s, 1H), 2.26 (s, 3H).

(L4). (E)-4-hydroxy-3-(4-hydroxyphenyl)acryloyl-6-methyl-2H-pyran-2-one. Yield: 21 %. M.p. = 210–215 °C. Found, %: C 65.90; H 4.27. Anal. Calcd. (%) for $C_{15}H_{12}O_5$: C 66.17; H 4.44. 1H NMR (400 MHz, DMSO) δ 18.08 (s, 1H), 10.35 (s, 1H), 8.01 (d, $J=15.7$ Hz, 1H), 7.88 (d, $J=15.7$ Hz, 1H), 7.59 (d, $J=8.5$ Hz, 2H), 6.87 (d, $J=8.5$ Hz, 2H), 6.25 (s, 1H), 2.25 (s, 3H).

Complexes of zirconium phthalocyanine with dha derivatives (scheme 3) were obtained by ligand exchange reaction similarly described in the work [5] for the dha. The $PcZr(L1–L4)_2$ are rich blue crystalline substances that are soluble in the most organic solvents (benzene, toluene, chloroform etc). The complexes were characterized by 1H NMR, UV-Vis spectroscopy and elemental analysis for metal.

The general method of synthesis of phthalocyanine complexes of zirconium with dha derivatives as out-of-plane ligands (scheme 3). 445 mg $PcZr(C_7H_{15}COO)_2$ (0.5 mmol) dissolved in 2 ml of toluene under heating; 1.2 mmol of dha derivatives (20 % excess) also dissolved in 2 ml of toluene under heating. Reagents were mixed and refluxed for 5 h, and then reaction mixture was cooled. The resulting crystalline precipitate was filtered and washed with large amount of acetone. Product was dried at 60 °C.

$PcZr(L1)_2$. Bis-[3-(2E,4E)-hexa-2,4-dienoyl-4-hydroxy-6-methyl-2H-pyran-2-onato] zirconium phthalocyaninat. Yield: 27 %. Found, %: Zr 8.91. Anal. Calcd. (%) for $C_{56}H_{38}N_8O_8Zr$: Z, 8.75. 1H NMR (400 MHz, $CDCl_3$) δ 9.57–9.00 (m, 8H), 8.32–7.93 (m, 8H), 6.60 (t, $J=17.7$ Hz, 2H), 6.20–5.93 (m, 2H), 5.87 (t, $J=12.3$ Hz, 2H), 5.44–5.17 (m, 3H), 4.79 (s, 1H), 1.99 (s, 6H), 1.76 (d, $J=6.7$ Hz, 6H).



Scheme 3.

PcZr(L2)₂. Bis-[4-hydroxy-6-methyl-3-((2E,4E)-5-phenylpenta-2,4-dienoyl)-2H-pyran-2-onato] zirconium phthalocyaninat. Yield: 72 %. Found, %: Zr 7.73. Anal. Calcd. (%) for C₆₆H₄₂N₈O₈Zr: Zr 7.82. ¹H NMR (400 MHz, CDCl₃) δ 9.80–9.07 (m, 8H), 8.50–7.94 (m, 8H), 7.66–7.12 (m, 10H), 6.89 (d, *J* = 62.1 Hz, 4H), 6.43–6.03 (m, 4H), 4.91 (s, 2H), 2.07 (s, 6H).

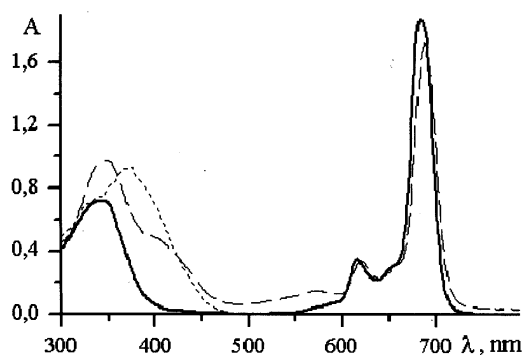
PcZr(L3)₂. Bis-[(E)-4-hydroxy-3-(3-(3-hydroxyphenyl)acryloyl)-6-methyl-2H-pyran-2-onato] zirconium phthalocyaninat. Yield: 39 %. Found, %: Zr 7.79. Anal. Calcd. (%) for C₆₂H₃₈N₈O₁₀Zr: Zr 7.96. ¹H NMR (400 MHz, DMSO) δ 9.61 (s, 2H),

9.40 (dd, *J* = 5.5, 3.0 Hz, 2H), 9.17–8.93 (m, 4H), 8.33 (dd, *J* = 5.8, 2.5 Hz, 2H), 8.22 (dd, *J* = 5.2, 3.3 Hz, 2H), 8.11 (dd, *J* = 8.0, 4.4 Hz, 4H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.20–7.08 (m, 3H), 7.08–6.90 (m, 3H), 6.78 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.53 (s, 1H), 6.12 (d, *J* = 15.5 Hz, 1H), 6.07 (d, *J* = 7.4 Hz, 2H), 4.85 (s, 2H), 3.36 (s, 2H), 2.01 (s, 6H).

PcZr(L4)₂. Bis-[(E)-4-hydroxy-3-(3-(4-hydroxyphenyl)acryloyl)-6-methyl-2H-pyran-2-onato] zirconium phthalocyaninat. Yield: 21 %. Found, %: Zr 7.74. Anal. Calcd. (%) for C₆₂H₃₈N₈O₁₀Zr: Zr 7.96. ¹H NMR (400 MHz, DMSO) δ 10.32 (s, 2H), 9.54–9.43 (m, 2H), 9.35–9.26 (m, 2H), 9.26–9.11 (m, 4H), 8.45–8.30 (m, 4H), 8.24–8.10 (m, 4H), 6.94 (d, *J* = 15.3 Hz, 2H), 6.72 (dd, *J* = 36.1, 8.4 Hz, 8H), 6.23 (d, *J* = 15.0 Hz, 2H), 4.86 (s, 2H), 2.02 (s, 6H).

The characteristic absorption bands of phthalocyanine compounds present in UV-Vis spectra of phthalocyanine complexes of zirconium with dha and its derivatives (figure) at the about 350 and 690 nm. A position of the Soret band of complexes with dha is typical for phthalocyanine systems, but in the case of PcZr(L1)₂ the Soret band is considerable broadened due to the superposition of the absorption maxima of the Soret band of phthalocyanine system and the absorption band of L1. In the spectra of PcZr(L2)₂–PcZr(L4)₂ complexes the Soret bands have shoulder in the red region of the spectrum (figure). Application of the method of expanding of the spectral bands into Gaussian components allowed distinguish the absorption maxima of the ligands in the complexes. The absorption maxima of ligands in complexes (except PcZr(L1)₂) are bathochromic shifted by 20–40 nm as compared with absorption bands of the free ligand.

¹H NMR spectra were recorded on a Varian VXR



UV-Vis spectra of PcZr(dha)₂ (solid), L4 (dot) and PcZr(L4)₂ (dash) in DMSO.

(300 MHz) spectrometer, internal standard — TMS, solvent — CDCl_3 or $\text{DMSO-}d_6$. The UV-Vis absorption spectra were obtained on a spectrometer Perkin Elmer UV/VIS Lambda 35 in quartz cuvettes with a thickness of the absorbent layer 10 mm in DMSO, the concentration of the substances was $5 \cdot 10^{-5}$ mol/l.

CONCLUSIONS. The dha derivatives with aldehydes and their complexes with zirconium phthalocyanine were obtained. In these complexes, two chromophores (phthalocyanine and dha derivatives) were combined into one macrocyclic molecule through the metal atom. An additional chromophore in the macrocyclic system appears in the UV-Vis absorption spectra by broadening of the Soret band, its bathochromic shift and presence of shoulder in the red region of the Soret band.

РЕЗЮМЕ. Синтезовано барвники на основі повідних дегідратетової кислоти її взаємодією з альдегідами. Ці барвники використано в синтезі нових фталоціанінових комплексів цирконію з позаплощинними лігандами. Методами ПМР-спектроскопії, ЕСП встановлено склад, будову та спектральні властивості отриманих сполук. Додатковий хромофор у макроциклічній системі проявляється в значному уширенні смуги Sore, її батохромному зсуві та появі плеча в червоній області ЕСП.

Ключові слова: дегідратетова кислота, фталоціанін цирконію, ЕСП.

РЕЗЮМЕ. Синтезированы красители на основе производных дегидратетовой кислоты ее конденсацией с альдегидами. Эти красители использованы в синтезе новых комплексов фталоцианина циркония с внеплоскостными лигандами. Состав, структура и спектральные свойства полученных соединений уста-

новлены с помощью ПМР и ЭСП. Дополнительный хромофор в макроциклической системе проявляется уширением полосы Sore, ее батохромным сдвигом и появлением плеча в красной области ЭСП.

Ключевые слова: дегидратетовая кислота, фталоцианин циркония, ЭСП.

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