OUT-OF-PLANE COORDINATED ZIRCONIUM(IV) AND HAFNIUM(IV) PHTHALOCYANINATES

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The article is devoted to methods of synthesis, the structure, and spectral characteristics of zirconium and hafnium phthalocyaninates with out-of-plane coordinated ligands. The general scheme for the synthesis of out-of-plane coordinated Zr and Hf phthalocyanines includes obtaining initial dichloride or dihydroxo complexes, which then undergo substitution reactions with β -dicarbonyl compounds, hydroxybenzoic, sulfo- and aliphatic carboxylic acids, etc. In the case of polyphenols, which are bidentate ligands, one ligand is coordinated to the central atom of the macrocycle. If β -dicarbonyl compounds or carboxylic acids are introduced into the reaction, two ligands are coordinated. The reactivity of the out-of-plane coordinated ligands of Zr and Hf phthalocyanines was also investigated. In all obtained out-of-plane coordinated Zr and Hf phthalocyanines, the ligands are located in the *cis* position relative to the plane of the phthalocyanine macrocycle. X-ray diffraction, NMR, and UV-Vis spectroscopy have proved this arrangement of ligands. According to the X-ray diffraction data of Zr and Hf dibenzoylmethanato phthalocyanines, the metal atom is out of the plane of the phthalocyanine macrocycle, which itself is not planar. The central atoms are located almost in the middle between the N4 planes of the phthalocyanine macrocycle and the O4 of the extraplanar ligands. The UV-Vis spectra of out-of-plane coordinated Zr and Hf phthalocyanines in organic solvents have a typical appearance for most metal phthalocyanines, characterized by a B-band of absorption in the region of 335–350 nm, a Q-band at 680–690 nm, and its satellite in the region of 615–620 nm. If the extraplanar ligand is a chromophore (e.g., curcumin or condensed derivatives of dehydroacetic acid), there are additional absorption bands in UV-Vis spectra located between the B- and Q-bands. The influence of the nature of the central metal atoms, ligands and solvents on the fluorescent properties of the out-of-plane coordinated Zr and Hf phthalocyanines was also discussed.

Keywords: phthalocyanines, zirconium, hafnium, synthesis, spectroscopy.

INTRODUCTION. The phthalocyanine macrocycle was first obtained by chance in 1907 [1] and its copper salt in 1927 [2] as a by-product of reactions of phthalic acid derivatives. The new unknown substance attracted attention because it had deep blue color, was thermally stable, and did not decompose in alkalis and acids. In 1934, Linstead showed that phthalocyanines are formed at high temperatures from various phthalic acid derivatives via the stage of formation of 1,2-dicyanobenzene, and that phthalocyanine itself is its tetramer and may contain a metal ion [3]. The following year, Robertson confirmed the structure and aromaticity of the phthalocyanine macrocycle by X-ray diffraction [4]. Subsequently, Linstead developed general methods for the synthesis of various phthalocyanine precursors, in particular, o-dinitriles [5–8], metal phthalocyanines [9–13], substituted phthalocyanines [14, 15], and their analogues [16–23]. To date, complexes of phthalocyanines with most metals and some nonmetals have been described [24].

Phthalocyanines are aromatic systems wherein the number of π -electrons in the conjugate system corresponds to Huckel's rule ($4n + 2$) and is 42 electrons. Their aromaticity is confirmed by the proximity of the bond lengths in the molecule: the bond length (C-N) in the macrocycle (1.35 Å) is close to the bond length in benzene nuclei (1.40 Å). At the same time, the bond length (C-C) between the macrocycle and benzene rings is significantly longer; it is 1.50 Å, which is close to the length of the σ -bond (1.54 Å). This indicates that the coupling between the π -electron systems of the macrocycle and benzene nuclei is weak. Thus, there are two quasi-autonomous aromatic sys-

tems of benzene nuclei and an aromatic macrocyclic system in the molecule [25]. The π -electron system of the phthalocyanine molecule is quite large; the difference in the energy level of HOMO and LUMO corresponds to the photon energy of the long-wavelength part of the spectrum. This causes a deep blue or green color of these compounds.

The aromaticity of phthalocyanines explains their high thermal and chemical stability and low tendency to open the conjugate macrocycle system [24]. The phthalocyanine macrocycle, as an aromatic system, undergoes electrophilic substitution reactions: chlorination, bromination, sulfochlorination, sulfonation, etc. However, these reactions result in a nonstoichiometric mixture of different isomeric compounds. Therefore, appropriate substituted o-dinitriles are generally used to produce peripherally substituted phthalocyanines. Nevertheless, individual compounds are formed only from symmetric o-dinitriles (for example, 4,5- or 3,6-substituted 1,2-dicyanobenzenes). In all other cases, mixtures of isomeric products are formed.

Phthalocyanine ligand is a dibasic, tetradentate acid. The cavity diameter of the phthalocyanine macrocycle is 3.65–4.50 Å [24], which is suitable for the coordination of most metal ions. If the valence of the metal ion in the phthalocyanine complex is more than two, or its coordination number is more than four, then such a central metal atom (CA) contains (or may contain) additional axial or out-of-plane ligands. In [24], some possible types of out-of-plane ligands coordinating to the phthalocyanine macrocycle are presented (Fig. 1).

Fig. 1. Molecular structures of different types of phthalocyanine complexes PcM_mX_n [24].

The high coordination numbers of the CA make it possible to form out-of-plane coordinated complexes of various compositions and structures. For example, carboxylate complexes are described for phthalocyanines of tin with coordination numbers (CN) 7 or 8 [26, 27] and phthalocyanines of Zr and Hf with CN 8, in which the carboxylate ligand can be bridged between two macrocyclic systems [28]. (Fig. 2). For phthalocyanines of Zr and Hf, out-of-plane coordinated complexes with a reasonably wide range of ligands are described.

Methods of synthesis of zirconium and hafnium phthalocyaninates with out-of-plane coordinated ligands. Zr and Hf phthalocyanine dichloride complexes were first obtained by

fusing 1,2-dicyanobenzene with the corresponding metal tetrachlorides [29]. However, it was found [30] that the reaction produces Zr and Hf phthalocyanines with a chlorinated macrocycle, which was assigned the formula $ClPcMCl_2$. It was later proved [31–33] that $ClPcMCl_2$ is not an individual compound, it is a statistical mixture of chlorinated phthalocyanines with different numbers of chlorine atoms in the molecule, which corresponds to the general formula $ClPcMCl_2$. This conclusion was confirmed by NMR spectra of bis-(acetylacetonato)phthalocyanines of Zr and Hf obtained from corresponding dichloride complexes described in [29, 30] and pure $PcMCl_2$ [31–33].

Fig. 2. Crystal structure of Sn didodecanoato phthalocyaninate, CN = 7 (A) [26]; Sn didecanoato phthalocyaninate, CN = 8 (B) [27]; Hf dinonanoato phthalocyaninate, CN = 8 (C) and Zr bis(dinonanoato phthalocyaninate), CN = 8 (D) [28].

The out-of-plane chlorine atoms in Zr and Hf phthalocyanines are quite “mobile”, they undergo hydrolysis to form corresponding dihydroxo complexes $\text{PcM}(\text{OH})_2$ [30, 32, 34, 35]. This feature was used for the synthesis of PcML (L = pyrocatechins) and PcML_2 (L = β -dicarbonyl compounds, hydroxybenzoic, sulfo- and aliphatic carboxylic acids, etc) [28, 36–38].

The general scheme for the synthesis of out-of-plane coordinated Zr and Hf phthalocyanines is presented in Fig. 3. In the case of polyphenols, which are bidentate ligands, one ligand is coordinated to the CA of the macrocycle with CN = 6. If β -dicarbonyl compounds or carboxylic acids are introduced into the re-

action, two ligands are coordinated [36–38] and the CN of the CA is 8 (Fig. 3). In this case, the carboxylic acid is a bidentate or bridging bidentate ligand [28].

According to the scheme shown in Fig. 3, out-of-plane coordinated Zr and Hf phthalocyanines with more complex ligands were also obtained [37, 39–44] (Fig. 4). The reactivity of out-of-plane coordinated ligands of Zr and Hf phthalocyanines was also investigated. It was found [37] that the “mobility” of the chlorine atom in the 3-chloro-2,4-pentanedionate ligand is very low (in contrast to free 3-chloro-2,4-pentanedione), so it does not interact with thiol-containing compounds

Fig. 3. Scheme of synthesis of some out-of-plane coordinated Zr and Hf phthalocyanines.

(Fig. 5, reaction A). As a result of complexing, the phthalocyanine macroring stabilizes the formed cyclic system of the β -diketonate ligand, and the mobility of the chlorine atom sharply decreases [28, 37]. During the reaction of the ester group, the formation of amides (Fig. 5, reaction B) was proved [28]. However, when a reaction with ammonia or hydrazine takes place, a mixture of indeterminate products is formed, or destruction of the macro-

cyclic system is observed. The synthesis reaction of Zr and Hf dibromide bis-(N-(5-pentanoato)-4-methyl-pyridiniumcarboxylato) phthalocyaninates proved to be quite indicative. When dichloride complexes of Zr and Hf phthalocyaninates react with N-(5-pentanoato)-4-methyl-pyridiniumcarboxylic acid bromide, a corresponding cationic complex is formed, but the anion is a mixture of chlorides and bromides (Fig. 5, reaction B).

Fig. 4. Out-of-plane coordinated derivatives of Zr and Hf phthalocyanines with: 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-onate (A) [39]; 2-(2,4-dioxopentan-3-ylthio)-N-(4-methoxyphenyl)acetamide (B) [40]; 2Z)-4-[(4-methylphenyl)-amino]-2-ovate (C) [37]; (4-[4-(2-[(2-methylphenyl)amino]-2-oxoethyl)thio]-3-dimethyl-1pyrazol-1-yl)benzoic (D) [37]; oxyquinolate (E) [41], curcuminat (F) [42], dehydroacetate and its condensed derivatives (G) [43, 44] as ligands, and clathrochelate (H) [45].

If the bis- ω -bromopentanoates of Zr and Hf phthalocyanines react with 4-methylpyridine individual cationic complexes are formed (Fig. 5, reaction D) [28, 37]. In [35], it was recommended to carry out similar reactions based on Zr and Hf dihydroxo phthalocyanines.

Structure of out-of-plane coordinated zirconium and hafnium phthalocyanines. In all out-of-plane coordinated Zr and Hf phthalocyanines, the ligands are located in the *cis* position relative to the plane of the phthalocyanine

macrocycle. This arrangement of ligands has been proven by X-ray diffraction, NMR, and UV-Vis spectroscopy [36–38, 46].

According to the X-ray diffraction data of Zr and Hf dibenzoylmethanato phthalocyanines, the CA of the metal is out of the plane of the phthalocyanine macrocycle, which itself is not planar [46]. The central atoms are located almost in the middle between the N4 planes of the phthalocyanine macrocycle and the O4 of the extraplanar ligands (Table 1).

Fig. 5. Reactivity of extraplanar ligands in Zr and Hf phthalocyanines.

The similarity of the structural parameters of Zr and Hf bis-(dibenzoylmethanato)phthalocyanines is observed (see Table 1). This similarity exists for the very close atomic radii of Zr and Hf ions due to lanthanide compression

[47]. This leads to the similarity of both structural parameters and other spectral characteristics, such as the position of signals in NMR spectra and absorption maxima in UV-Vis spectra [46].

Table 1

Selected parameters of bond lengths and distances to the planes N4 and O4 of Zr and Hf bis-(dibenzoylmethanato)phthalocyanines.

Bond	Length, Å	Angle	ω , degree	Distance to the plane, Å
Zr - O	2.1610(16) - 2.1807(16)	O - Zr - O	71.41 – 74.52	1.184
Hf - O	2.1577(14) - 2.1719(14)	O - Hf - O	70.99 – 74.91	1.181
Zr - N	2.282(2) - 2.303(2)	N - Zr - N	73.35 – 74.26	1.211
Hf - N	2.2641(17) - 2.2919(16)	N - Hf - N	73.58 – 74.58	1.194

Most of the described out-of-plane coordinated Zr and Hf phthalocyanines were investigated by NMR spectroscopy. As concerns the complexes with pyrocatechinate and sulfosalicylate ligands, their solubility is too low for accurate NMR studies [36]. However, complexes of Zr and Hf phthalocyanines with β -diketones, β -ketoethers, and carboxylic acids as extraplanar ligands have been studied extensively [39, 48–50]. In the case of β -dicarbonyl complexes, the coordination of two ligands to the CA of the macrocycle was established. Proton signals in the NMR spectra can be divided into two groups [48]. The first group is the signals of phenyl protons of the phthalocyanine macrocycle located in the region of 9.5–8.0 ppm. Their position and morphology of multiplets are similar to the data given in the literature for β -dicarbonyl phthalocyanine complexes of thorium and uranium [51]. The second group is proton signals of extraplanar ligands. They are always upfield shifted compared to uncoordinated ligands. Analysis of NMR spectre data for pairs of complexes (Zr-Hf) with the identical ligands shows that the CA has almost no effect on the position of the signals in the spectra because they have very similar values [36, 37, 46]. In the case of complexes with asymmetric β -dicarbonyl ligands, the formation of a mixture of *cis*- and *trans*-isomers has been proved [36, 48] (Fig. 6).

Fig. 6. Coordination of asymmetric β -diketones to the CA of the phthalocyanine macrocycle with the formation of a mixture of isomers.

Spectral characteristics. The UV-Vis spectra of out-of-plane coordinated Zr and Hf phthalocyanines in organic solvents have a typical appearance for most metal phthalocyanines, characterized by a B-band of absorption in the region of 335–350 nm, a Q-band of 680–690 nm, and its satellite in the region of 615–620 nm (Table 2) [36–38]. If the extraplanar ligand is a chromophore (e.g., curcumin or condensed derivatives of dehydroacetic acid), there are additional absorption bands in the UV-Vis spectra located between the B- and Q-bands [38, 42, 44].

Table 2

UV-Vis data of out-of-plane coordinated Zr and Hf phthalocyanines in toluene.

M	Ligand	λ , nm (log ϵ)		
		B-band	Q-satellite	Q-band
Zr		342 (4.72)	618 (4.44)	686 (5.18)
Hf		349 (4.70)	618 (4.38)	688 (5.19)

Table 2

M	Ligand	λ , nm (log ϵ)		
		B-band	Q-satellite	Q-band
Zr		343 (4.88)	617 (4.54)	688 (5.28)
Hf		349 (4.89)	620 (4.56)	690 (5.28)
Zr		344.6 (4.78)	617.2 (4.58)	684.9 (5.29), 688.1 (5.29) d
Hf		340.9 (4.82)	616.7 (4.61)	684.2 (5.37), 686.8 (5.38) d
Zr		340.0 (5.05)	617.0 (4.56)	656.0 (4.48), 683.0 (5.31) w
Hf		340.0 (5.05)	617.0 (4.54)	655.0 (4.48), 683.0 (5.30) w
Zr		336.1 (4.63)	618.8(4.29)	685.2 (5.00), 689.4(5.00) d
Hf		345.0 (4.74)	619.4 (4.40)	682.1 (5.08), 693.3 (5.09) d
Zr		342.8 (4.58)	618.2 (4.30)	686.4 (5.13) w
Hf		342.8 (4.53)	616.9 (4.27)	684.9 (5.17) w
Zr		341.7 (4.80)	617.1 (4.52)	654.7 (5.28), 685.0 (5.31) w
Hf		337.1 (4.87)	616.3 (4.61)	683.7 (5.57), 685.6 (5.57) w
Zr		341.7 (4.85)	618.1 (4.52)	686.9 (5.27) w
Hf		339.5 (4.78)	616.2 (4.42)	684.1 (5.22) w
Zr	C ₇ H ₁₅ CO ₂ H	341	620 sh	684
Hf		340	616 sh	684

In the case of water-soluble Zr and Hf phthalocyanines, such as sulfosalicylate, galate, chromotropic and amino acids, absorption bands characteristic of phthalocyanine aggregates are observed in water [52].

The authors showed [46, 48, 49] that in some cases broadening or splitting of the Q-band in the UV-Vis spectra of β -diketonate and β -ketoester complexes is observed. Such spectral characteristics are untypical of phthalocyanine complexes and associated with a significant

decrease in molecule symmetry, proving the *cis*-coordination of the ligands relative to the plane of the phthalocyanine macrocycle.

In [50], the luminescent properties of Zr and Hf phthalocyanines with extraplanar ligands in various solvents were investigated. Analyzing the experimental data, the authors concluded that the heavy central metal atom reduces the fluorescence intensity of the complexes. For example, in the series Zn, Zr, Hf, the highest fluorescence is shown by zinc phthalocyanine

(0.200 in DMSO), the quantum yield of fluorescence of Zr phthalocyanine is about an order of magnitude lower (Table 3), and Hf complexes do not fluoresce, or their fluorescence is very low. The highest Stokes shift is 20 nm which is typical of phthalocyanine complexes.

The influence of the nature of the ligands and solvents on the quantum yield of fluorescence and the lifetime of excited states in out-of-plane coordinated Zr phthalocyanines was also established. The lowest fluorescence quantum yield was observed for Zr phthalocyanine dichloride (in DMSO it is 0.006), and for the

complex of Zr phthalocyanine with 4-benzoyl-3-methyl-1-phenyl-1H-pyrazole-5(4H)-one it is 0.073 (Table 3). Slightly lower quantum yields were also observed for carboxylate complexes of Zr phthalocyanine in comparison with β -diketonate [39, 46, 49, 50]. Regarding the nature of the solvent, in toluene, the largest values of the molar extinction coefficient and the smallest values of the lifetime of the excited state were observed. At the same time, the highest values of the quantum yield of fluorescence and the lifetime of the excited state were obtained in DMSO (Table 3).

Table 3

Fluorescence data of out-of-plane coordinated PcZrL_2 .

L	Solvent	λ_F , nm	Φ_F	$\Delta\lambda$	τ , ns
toluene	708	0.054	20	1.66
	DMSO	702	0.073	18	6.33
toluene	702	0.063	16	2.58
	DMSO	700	0.075	18	8.87
toluene	701	0.042	13	1.66
	DMSO	703	0.072	17	5.42
toluene	695	0.004	13	1.27
	DMSO	697	0.069	12	5.72
toluene	693	0.010	10	
	DMSO	695	0.020	8
toluene	708	0.073	17	1.99
	DMSO	709	0.063	15	5.79
toluene	697	0.009	13	9.08
	DMSO	703	0.013	15	8.46

Prospects for application. Phthalocyanine complexes are widely used in many fields of science and technology [53]. The areas of their application can be divided into two groups. The first group is based on the use in a homogeneous phase, such as in photodynamic therapy, catalysis, etc. The second one is based on transformations at the phase boundary, as in sensors, photovoltaic cells, and others. Depending on the chemical nature of the extraplanar ligand, the prospects of its application are studied in different fields. Zr and Hf bis-(β -diketonato)phthalocyanines due to high electrochemical stability, fluorescence properties [46, 49, 50], and prominent electrochromism are promising for use as sensors and the creation of photovoltaic [40, 54, 55] and OLED elements [56–58]. Watersoluble complexes with citrate, lysinate, sulfosalicylate and other ligands show high cytostatic and cytotoxic activity and can be proposed as agents for the photodynamic and dark therapy of malignant neoplasms [59, 60]. The complexes containing a free amino or carboxy group in extraplanar ligands show high antimicrobial activity in the composite cement with graphite oxide used in dentistry [61, 62]. Zr and Hf phthalocyanines with extraplanar ligands can inhibit or redirect the fibril formation of proteins associated with neurodegenerative diseases [63–67].

CONCLUSIONS. Thus, it is shown that the coordination of out-of-plane ligands to the central metal atom in Zr and Hf phthalocyanines makes it possible to change their physicochemical properties in a targeted manner. This approach is much simpler than the in-

roduction of substituents on the periphery of the phthalocyanine macrocycle. It opens up prospects for using out-of-plane coordinated Zr and Hf phthalocyanines as photosensitive, electrochromic, photoelectrocatalytic materials. Hydrophilic groups in the out-of-plane ligands provide their biological activity and the possibility of use as antitumor, antimicrobial agents.

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ПОЗАПЛОЩИННО КООРДИНОВАНІ ФТАЛОЦІАНІНАТИ ЦИРКОНІЮ(IV) І ГАФНІЮ(IV)

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Статтю присвячено методам синтезу, будові та спектральним характеристикам фталоціанінатів цирконію та гафнію з позаплощинно координованими лігандами. Наведено загальну схему синтезу позаплощинно координованих фталоціанінів Zr та Hf. Методами РСА, ЯМР та ЕСП показано, що в усіх отриманих позаплощинно координованих фталоціанінах Zr і Hf ліганди розташовані в цис-положенні щодо площини макроциклу. Атом металу виходить із площини макроциклу фталоціаніну і розташований майже посередині між площинами N4 макроциклу фталоціаніну та O4 позаплощинних лігандів. ЕСП позаплощинно координованих фталоціанінів Zr та Hf в органічних розчинниках мають типовий вигляд для фталоціанінів металів, що характеризується В-смугою поглинання в області 335–350 нм, Q-смугою – 680–690 нм, та коливальним супутником при 615–620 нм. Якщо позаплощинний ліганд є хромофором (наприклад, куркумін

або конденсовані похідні дегідрацетової кислоти), у ЕСП спостерігаються додаткові смуги поглинання, що знаходяться між В- та Q-смугами. Також обговорено вплив центрального атома металу, лігандів та розчинників на флуоресцентні властивості позаплощинно координованих фталоціанінів Zr та Hf.

Ключові слова: фталоціаніни, цирконій, гафній, синтез, спектроскопія.

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