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Synthesis, structure, spectroscopic properties, and electrochemical behavior of mixed ligand bis(β-ketoesterato)zirconium (IV) and -hafnium (IV) phthalocyaninates

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Abstract

The synthesis of new zirconium and hafnium mixed ligand phthalocyanine complexes $PcM(\beta-ketoester)_2$, where M-Zr (IV), Hf (IV); Pc – the dianion of phthalocyanine, and β -ketoester – the out planed ligand, is reported. The obtained complexes are characterized by ¹H NMR, IR, UV–Vis spectroscopy and cyclic voltammetry. ¹H NMR and elemental analysis confirm the substitution of two Cl atoms for two β -ketoester fragments to the central atom of the macrocycle. The data of ¹H NMR, UV–Vis spectroscopy have allowed us to conclude that two β -ketoester ligands are in the *cis* geometry to the phthalocyanine plane. X-ray crystallography for bis(isopropyl 3-oxobutanoato)hafnium(IV)phthalocyanine confirms this conclusion. The central macrocycle of the phthalocyanine ligand is not exactly planar (deviations from the least-square plane exceed 0.15 Å) and has the conformation of an essentially flattened *crown*. The Hf(1) atom is 1.349(3) above this least-square plane. Cyclic voltammetry investigation shows that the introduction of two β -ketoester ligands to the central atom of phthalocyanine complex leads to both chemical and electrochemical stabilization of the whole Pc system. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

For the past decades, phthalocyanine (Pc) complexes have been the focus of a steady interest from researchers due to their unique physico-chemical properties: catalytic, photoconductive, and nonlinear optical [1-5]. They allow one to apply phthalocyanine derivatives in different fields of science and technology – from electronic and catalysis to medicine [6]. Introduction of the substituents on the periphery of the Pc macrocycle and/or directly to the central metal atom can change both electronic and physicochemical properties of the Pc system as a whole.

The study of the redox characteristics of phthalocyanine complexes is a timely topic since such data allow us to carry out a targeted search for substances potentially having catalytic activity [4]. Furthermore, oxidation/reduction of phthalocyanine complexes makes it possible to change their optical properties, which may be used in designing both new electrochromic [1], photoconductive [2,3], and semiconductor [4] materials, as well as various devices such as displays or indicator panels [5].

It is known that the phthalocyanines with metals of the IVB group easily coordinate one or two out planed ligands

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Fig. 1. Scheme of synthesis of the mixed-ligand metallophthalocyanine complexes with β-ketoesters.

to the central atom [7]. The present work is dedicated to the synthesis, structure, spectroscopic characterization, and redox properties of novel mixed-ligand complexes of zirconium (IV) and hafnium (IV) phthalocyanines with β -ketoesters as out-planed ligands: methyl 3-oxobutanoate (1), ethyl 3-oxobutanoate (2), isopropyl 3-oxobutanoate (3), *tert*-butyl 3-oxobutanoate (4), ethyl 3-oxohexanoate (5), ethyl 3-oxo-3-phenylpropanoate (6), ethyl 2-oxo-1-cyclopentancarboxylate (7) (Fig. 1).

2. Experimental

2.1. General

All reactions were carried out under atmospheric conditions (Fig. 1). Toluene, *o*-xylene, hexane and chloroform were obtained commercially and used without further purification; β -ketoesters were used as received. Initially dichloro(phthalocyaninato) zirconium (IV) and hafnium (IV) were prepared by the reaction of ZrCl₄ (HfCl₄) with phthalodinitrile by published procedures [8]. IR spectra were recorded on a Specord M-80 spectrometer as KBr pellets. ¹H NMR spectra were recorded on a Varian (300 MHz) spectrometer (CDCl₃/TMS). The UV–Vis absorption spectra were obtained on a Specord M-40 in $CDCl_3$ (l = 1 mm).

2.2. Synthesis

2.2.1. Bis(methyl 3-oxobutanoato)zirconium (IV) and -hafnium (IV) phthalocyanines (complexes 1a,b)

A 0.74 mmol sample of PcMCl₂ was suspended in 10 ml of xylene, and 1.67 mmol of methyl 3-oxobutanoate was added. The reaction mixture was heated at 140 °C for 6 h under reflux (evolution in HCl). The hot solution was filtered for separation from the starting materials. The resulting solution was cooled to room temperature and the formed crystals (bis(β -ketoesterato)phthalocyanine complex of metal) were separated and washed abundantly with hexane. Hexane was added to the solution if necessary. Thus, an additional quantity of the product was obtained. All synthesized complexes were first air dried, and after that dried in vacuum at 60 °C for 8 h. Compound **1a**: Yield is 40%. *Anal.* Calc. for C₄₂H₃₀N₈O₆Zr: C, 60.49; H, 3.63; N, 13.44; Zr 10.92. Found: C, 61.05; H, 3.25; N, 13.10; Zr, 11.10%.

Compound **1b**: yield is 41%. *Anal.* Calc. for $C_{42}H_{30}N_8O_6Hf$: C, 54.56; H, 3.28; N, 12.16; Hf, 19.40. Found: C, 54.15; H, 3.25; N, 11.95; Hf, 19.50%.

2.2.2. Bis(ethyl 3-oxobutanoato)zirconium (IV) and -hafnium (IV) phthalocyanines (complexes 2a,b)

Synthesis was carried out by an analogous method as for **1a,b** using PcMCl₂ and ethyl 3-oxobutanoate as starting reagents. Compound **2a**: yield is 39%. *Anal*. Calc. for $C_{44}H_{34}N_8O_6Zr$: C, 61.31; H, 3.98; N, 13.00; Zr 10.57. Found: C, 61.85; H, 3.80; N, 12.70; Zr, 10.80%. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 9.46–9.10 (m, Pc, 8H), 8.10–7.95 (m, Pc, 8H), 3.57 (m, 2CH, 2H), 3.54–3.40 (m, CH₂, 2H), 3.09–2.84 (m, CH₂, 2H), 1.29 (t, CH₃, 3H), 1.07 (t, CH₃, 3H), 0.96 (t, CH₃, 3H), 0.75 (t, CH₃, 3H).

Compound **2b**: yield is 37%. *Anal.* Calc. for $C_{44}H_{34}N_8O_6Hf$: C, 54.56; H, 3.28; N, 12.16; Hf, 19.40. Found: C, 54.15; H, 3.25; N, 11.95; Hf, 19.50%. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 9.50–9.36 (m, Pc, 8H), 8.13–8.09 (m, Pc, 8H), 3.56 (m, 2CH, 2H), 3.54–3.44 (m, CH₂, 2H), 3.12–2.84 (m, CH₂, 2H), 1.30 (t, CH₃, 3H), 1.07 (t, CH₃, 3H), 0.96 (t, CH₃, 3H), 0.77 (t, CH₃, 3H).

2.2.3. Bis(isopropyl 3-oxobutanoato)zirconium (IV) and -hafnium (IV) phthalocyanines (complexes 3a,b)

A 0.74 mmol sample of PcMCl₂ was suspended in 10 ml toluene, and 1.67 mmol of isopropyl 3-oxobutanoate was added. The reaction mixture was heated at 116 °C for 3-5 h under reflux (evolution in HCl). The hot solution was filtrated for separation from the starting materials. Hexane was added to the resulting solution and it was cooled to room temperature. The formed crystals (bis(β-ketoesterato)phthalocyanine complex of metal) were separated and washed abundantly with hexane. All synthesized complexes were first air dried, and after that dried in vacuum at 60 °C for 8 h. Compound 3a: yield is 30%. Anal. Calc. for C₄₆H₃₈N₈O₆Zr: C, 62.07; H, 4.30; N, 12.59; Zr, 10.24. Found: C, 62.35; H, 4.40; N, 12.20; Zr, 10.30%. ¹H NMR (300 MHz, CDCl₃) δ, ppm: 9.51–9.29 (m, Pc, 8H), 8.15-8.07 (m, Pc, 8H), 4.16 (m, CH, H), 3.97 (m, CH, H), 3.55 (dd, 2CH, 2H), 1.52 (d, CH₃, 3H), 1.31 (d, CH₃, 3H), 1.12 (s, CH₃, 3H), 0.89 (s, CH₃, 3H), 0.23 (d, CH₃, 3H), 0.12 (d, CH₃, 3H).

Compound **3b**: yield is 28%. *Anal.* Calc. for $C_{46}H_{38}N_8O_6Hf$: C, 56.53; H, 3.92; N, 11.46; Hf, 18.24. Found: C, 56.65; H, 4.05; N, 11.05; Hf, 18.20%. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 9.49–9.30 (m, Pc, 8H), 8.15–8.08 (m, Pc, 8H), 4.10 (m, CH, H), 3.93 (m, CH, H), 3.49 (dd, 2CH, 2H), 1.53 (d, CH₃, 3H), 1.27 (d, CH₃, 3H), 1.12 (s, CH₃, 3H), 0.89 (s, CH₃, 3H), 0.22 (d, CH₃, 3H), 0.09 (d, CH₃, 3H).

2.2.4. The synthesis of bis(tret-butyl 3oxobutanoato)zirconium (IV) and -hafnium (IV) phthalocyanines (complexes 4a,b)

The synthesis was carried out by an analogous method as for **3a,b** using PcMCl₂ and *tert*-butyl 3-oxobutanoate as starting reagents. Compound **4a**: yield is 30%. *Anal.* Calc. for C₄₈H₄₂N₈O₆Zr: C, 62.79; H, 4.61; N, 12.20; Zr, 9.92. Found: C, 62.95; H, 4.45; N, 12.00; Zr, 9.90%. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 9.43–9.39 (m, Pc, 8H), 8.21-8.17 (m, Pc, 8H), 3.55 (s, CH, H), 3.36 (s, CH, H), 1.57 (s, 3CH₃, 9H), 1.48 (s, CH₃, 3H), 1.43 (s, CH₃, 3H), 0.54 (s, CH₃, 3H), 0.43 (s, 2CH₃, 6H).

Compound **4b**: yield is 29%. *Anal.* Calc. for $C_{48}H_{42}N_8O_6Hf$: C, 57.34; H, 4.21; N, 11.15; Hf, 17.72. Found: C, 57.55; H, 4.25; N, 11.05; Hf, 17.75%. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 9.40–9.35 (m, Pc, 8H), 8.20–8.13 (m, Pc, 8H), 3.51 (s, CH, H), 3.34 (s, CH, H), 1.54 (s, 3CH₃, 9H), 1.45 (s, CH₃, 3H), 1.41 (s, CH₃, 3H), 0.53 (s, CH₃, 3H), 0.43 (s, 2CH₃, 6H).

2.2.5. Bis(ethyl 3-oxohexanoato)zirconium (IV) and -hafnium (IV) phthalocyanines (complexes 5a,b)

The synthesis was carried out by an analogous method as for **3a,b** using PcMCl₂ and ethyl 3-oxohexanoate as starting reagents. Compound **5a**: yield is 24%. *Anal.* Calc. for C₄₈H₄₂N₈O₆Zr: C, 62.79; H, 4.61; N, 12.20; Zr, 9.92. Found: C, 63.05; H, 4.65; N, 12.10; Zr, 9.95%. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 9.31–9.28 (m, Pc, 8H), 8.16– 8.13 (m, Pc, 8H), 3.49 (m, 2CH, 2H), 3.05 (m, CH₂, 2H), 2.87 (m, CH₂, 2H), 1.59 (s, 2CH₃, 6H), 1.29 (m, CH₂, 2H), 0.93 (m, CH₂, 2H), 0.64 (m, CH₂, 2H), 0.43 (t, CH₃, 3H), 0.23 (m, CH₂, 2H), 0.09 (t, CH₃, 3H).

Compound **5b**: yield is 26%. *Anal.* Calc. for $C_{48}H_{42}N_8O_6Hf$: C, 57.34; H, 4.21; N, 11.15; Hf, 17.72. Found: C, 57.45; H, 4.30; N, 10.95; Hf, 17.65%. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 9.33–9.27 (m, Pc, 8H), 8.18–8.16 (m, Pc, 8H), 3.42 (m, 2CH, 2H), 3.01 (m, CH₂, 2H), 2.83 (m, CH₂, 2H), 1.59 (s, 2CH₃, 6H), 1.30 (m, CH₂, 2H), 0.93 (m, CH₂, 2H), 0.64 (m, CH₂, 2H), 0.54 (m, CH₂, 2H), 0.39 (t, CH₃, 3H), 0.08 (t, CH₃, 3H).

2.2.6. Bis(ethyl 3-oxo-3-phenylpropanoato)zirconium (IV) and -hafnium (IV) phthalocyanines (complexes 6a,b)

The synthesis was carried out by an analogous method **3a,b** using PcMCl₂ and ethyl 3-oxo-3-phenylpropanoate as starting reagents. Compound **6a**: yield is 25%. *Anal.* Calc. for $C_{54}H_{38}N_8O_6Zr$: C, 65.77; H, 3.88; N, 11.36; Zr, 9.24. Found: C, 66.00; H, 3.95; N, 11.10; Zr, 9.20%. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 9.69–9.09 (m, Pc, 8H), 8.28–8.06 (m, Pc, 8H), 7.83 (m, C₆H₅, H), 7.71 (m, C₆H₅, H), 7.12 (d, C₆H₅, 4H), 6.78–6.68 (dd, C₆H₅, 4H), 4.39 (dd, 2CH, 2H), 3.85 (m, CH₂, 2H), 3.22 (m, CH₂, 2H), 0.97 (tt, 2CH₃, 6H).

Compound **6b**: yield is 25%. *Anal.* Calc. for $C_{54}H_{38}N_8O_6Hf$: C, 60.42; H, 3.57; N, 10.44; Hf, 16.51. Found: C, 60.85; H, 3.90; N, 10.10; Hf, 16.60%. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 9.58–9.14 (m, Pc, 8H), 8.29–8.04 (m, Pc, 8H), 7.80 (m, C₆H₅, H), 7.73 (m, C₆H₅, H), 7.10 (d, C₆H₅, 4H), 6.77–6.69 (dd, C₆H₅, 4H), 4.35 (dd, 2CH, 2H), 3.82 (m, CH₂, 2H), 3.16 (m, CH₂, 2H), 0.96 (tt, 2CH₃, 6H).

2.2.7. Bis(ethyl 3-oxo-1-cyclopentancarboxylato)zirconium (IV) and -hafnium (IV) phthalocyanines (complexes 7*a*,*b*)

The synthesis was carried out by an analogous method **3a,b** using PcMCl₂ and ethyl 3-oxo-1-cyclopentancarboxy-

late as starting reagents. Compound **7a**: yield is 28%. *Anal.* Calc. for $C_{48}H_{38}N_8O_6Zr$: C, 63.07; H, 4.19; N, 12.26; Zr, 9.99. Found: C, 63.30; H, 4.25; N, 12.10; Zr, 9.20%. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 9.42–9.22 (m, Pc, 8H), 8.14–8.03 (m, Pc, 8H), 3.84 (m, 2CH, 2H), 3.70 (m, CH₂, 2H), 2.95(q, C₅H₅, 2H), 2.38–2.27 (m, C₅H₅, 4H), 1.68 (m, C₅H₅, 4H), 1.05 (tt, 2CH₃, 6H).

Compound **7b**: yield is 29%. *Anal.* Calc. for $C_{48}H_{38}N_8O_6Hf$: C, 57.57; H, 3.83; N, 11.19; Hf, 17.80. Found: C, 57.75; H, 3.90; N, 11.10; Hf, 17.70%.¹H NMR (300 MHz, CDCl₃) δ , ppm: 9.40–9.21 (m, Pc, 8H), 8.11–8.03 (m, Pc, 8H), 3.81 (m, 2CH, 2H), 3.72 (m, CH₂, 2H), 2.92 (q, C₅H₅, 2H), 2.35–2.27 (m, C₅H₅, 4H), 1.65 (m, C₅H₅, 4H), 1.03 (tt, 2CH₃, 6H).

2.3. Crystallography

Complex **3b** was recrystallized from a mixture of xylene– hexane to obtain the respective single crystals suitable for X-ray diffraction. All crystallographic measurements were performed at 120 K on a Bruker SMART 6 K CCD diffractometer. The intensity data were collected within the range $1.6 < \theta < 28.3^{\circ}$ (-18 < h < 18, -30 < k < 30, -20 < l < 16) using graphite monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). The intensities of 39404 reflections (11688 unique, $R_{int} = 0.061$) were measured. Data were corrected for Lorentz and polarization effects and an absorption correction using the sADABS procedure [9] was applied. The crystallographic data of the complex are listed in Table 1.

The structure was solved by direct methods and refined by the full-matrix least-squares technique in the anisotropy approximation using the CRYSTALS program package [10]. In the refinement, 7596 reflections with $I > 3\sigma(I)$ were used. All hydrogen atoms were located in different Fourier maps (only H of the xylene solvate molecule were placed geomet-

Table 1

X-ray Structure Determination of the bis(isopropyl 3-oxobutanoato)hafnium (IV) phthalocyanine.1/2 Xylene (**3b**) – crystallographic data

	6 1
Empirical formula	C ₅₀ H ₄₃ HfN ₈ O ₆
Formula weight	1030.4
Temperature (K)	120
Crystal system	monoclinic
Space group	$P2_1/n$ (N 14)
Unit cell dimensions	
a (Å)	13.8503(3)
b (Å)	11.0812(2)
<i>c</i> (Å)	22.9810(6)
β (°)	102.649(1)
$V(\text{\AA}^3)$	4721.2(2)
Ζ	4
$D_{\rm calc} ({\rm g/cm}^3)$	1.45
$\mu (\mathrm{sm}^{-1})$	2.27
F (000)	2076
Crystal size (mm)	$0.03 \times 0.06 \times 0.10$
Reflections collected (R_{int})	39404/11688 (0.061)
R	0.039
$R_{ m w}$	0.041
Goodness-of-fit	1.078

rically) and included in the final refinement with fixed positional and thermal parameters. Convergence was obtained at R = 0.039 and $R_w = 0.041$, GOF = 1.078 (586 refined parameters; obs./variabl. 13.0). Chebushev weighting scheme [11] with parameters 0.68, -1.06, 0.07, -0.57, and -0.25 was used.

2.4. Electrochemical studies

Cyclic voltammograms were recorded in the range from -1.6 to +1.8 V using a PI-50.1 potentiostat coupled with a B7-45 tera-ohmic potentiometer as a current-voltage converter. The electrochemical measurements were made according to a three-electrode scheme: as the working electrode, we used a platinum ultramicroelectrode of diameter 10 µm; as the auxiliary electrode we used a platinum plate of area 1 cm²; the reference electrode was a silver chloride electrode connected to the test solution through a bridge with the supporting electrolyte. As the supporting electrolyte, we used a 0.1 M solution of Et₄NBF₄ in dichloromethane, purified according to the procedure in [12]. All the potentials presented are given relative to the internal standard, the redox pair Fc⁺/Fc, the halfwave potential of which was 645 mV in dichloromethane relative to the reference electrode used (630 mV relative to the standard hydrogen electrode (SHE) [13]). The range of potentials available for the studies was -2250 mV to 1360 mV. The uncertainty in the potential measured was $\pm 2 \text{ mV}$. The potential scan was set using a PI 50.1 potentiostat, the current was recorded using a V 7-45 high-resistance voltmeter, the voltage-current curves were recorded using an XY Recorder A3 recording device. The potential scanning rate was 10 mV/s, which corresponds to the conditions close to steady-state conditions for the given ultramicroelectrode. A feature of this method, in contrast to cyclic voltammetry using a large diameter (>25 μ m) working electrode, is the absence of peaks on the voltage-current curve [14].

3. Results and discussion

3.1. Synthesis

If the β -diketonato complexes of metallophthalocyanines are known and there are numerous methods for preparing them [7b,15], then the β -ketoesterato complexes of metallophthalocyanines have been synthesized first. β -Ketoesters form a fewer tautomers than β -diketones [16]. The solvent, concentration, and the substituents in α - and γ -positions influence enolization of the β -ketoesters significantly. At the same time the substituent in the ester group does not affect enolization [16b]. Increasing of temperature leads to a negligible decrease of the enol content [16c]. In contrast to β -diketones, increasing the concentration of β -ketoesters in solution leads to the sharp decrease of the *cis*-enol content. Considering that the complex formation takes place with the participation of *cis*-enol, it is very important to choose the reaction conditions. The reaction between $PcMCl_2$ and β -ketoesters is shown in Fig. 1 and it has been performed in xylene (for complexes 1a,b-2a,b) and in toluene (for complexes 3a,b-7a,b), because of the limited solubility of bis(methyl 3-oxobutanoato)- and bis(ethyl 3-oxobutanoato)zirconium (IV) and -hafnium (IV) phthalocyanines (1a, 1b, 2a, 2b) in toluene. It has been established that the presence of HCl acceptor (pyridine, triethylamine) does not influence the reaction rate and the product yield.

All synthesized compounds are fine crystalline substances that dissolve in most organic solvents (benzene, toluene, chloroform and others) in contrast to the starting complexes. The solubility of bis(β -ketoesterato)zirconium (or hafnium) phthalocyanine complexes depends to a considerable extent on the introduced β -ketoester ligands in the axial position. It is necessary to point out in the increase of the solubility of the obtained complexes in the row of ligands from 1 to 7 both for zirconium and hafnium complexes. Thus, if complexes 1a,b (with ligand 1 – methyl 3-oxobutanoate) are partially soluble in benzene, toluene, chloroform, then complexes 7a,b (with ligand 7 – ethyl 2-oxo-1-cyclopentancarboxylate) are highly soluble in these solvents that we have had some difficulties with isolation.

3.2. Structure

Peculiarities of the molecular and crystal structure of bis(isopropyl 3-oxobutanoato)hafnium (IV) phthalocyanine (3b) have been studied by single crystal X-ray diffraction. The perspective view of the molecule bis(isopropyl 3-oxobutanoato)hafnium (IV) phthalocyanine and selected geometrical parameters are given in Fig. 2. The Hf(1) atom has a slightly distorted octahedral coordination, the bond angles at this atom vary in the comparatively narrow ranges of 70.7-80.1(1), 109.8-118.9(1), and 140.4-143.5(1)°. The Hf(1)-O 2.213-2.126(3), avg. 2.169 and Hf(1)-N 2.278-2.303(4), avg. 2.290 Å distances are not unexceptional [17]. The central N(1-8)C(1)C(8)C(9)C(16)C(17)C(24)-C(25)C(32) macrocycle of the phtalocyanine ligand is not exactly planar (deviations from the least-square plane exceed 0.15 Å) and has the conformation of an essentially flattened crown. The Hf(1) atom is 1.349(3) above this least-square plane (Fig. 3). The dihedral angles between N(1)N(3)N(5)N(7) plane and planar bicyclic systems N(1)C(1-8), N(3)C(9-16), N(5)C(17-24), and N(7)C(25-32) are 161.0°, 168.5°, 172.3°, and 173.4°, respectively. The six-membered HfO₂C₃ heterocycles formed by the Hf and β -ketoesters have the conformation of a flattened *boat*.



Fig. 2. "Top" view and labelling scheme for the molecule of bis(isopropyl 3-oxobutanoato)hafnium (IV) phthalocyanine (**3b**.) Selected bond lengths (Å): Hf(1)-O(1) 2.126(3), Hf(1)-O(2) 2.213(3), Hf(1)-O(4) 2.122(3), Hf(1)-O(5) 2.216(3), Hf(1)-N(1) 2.278(4), Hf(1)-N(3) 2.294(4), Hf(1)-N(5) 2.284(4), Hf(1)-N(7) 2.303(4).



Fig. 3. "Side" view of complex 3b, solvent molecule and all hydrogen atoms have been omitted for clarity.

3.3. Spectral features

3.3.1. ¹H NMR spectra

¹H NMR data and elemental analysis suggest that two β-ketoester ligands are coordinated to the central atom of the macrocycle. The ¹H NMR spectra of bis(β -ketoesterato)zirconium (or hafnium) phthalocyanine complexes are sufficiently intricate and their signals can be divided into two parts: the signals of phthalocyanine protons (^aH -9.70-9.05; ^{β}H -8.30-8.00 ppm.) and the signals of β ketoester ligands protons. The signals of the out planed ligand protons are shifted upfield by the phthalocyanine ring current and have sufficient complex morphology (Fig. 4) (Table 2). If we compare with the spectra of free β-ketoester, for example, isopropyl 3-oxobutanoate (Fig. 4), and its metallophthalocyanine complex we can notice that free β -ketoester exists in 98–100% as the ketoform; at the same time, β -ketoester fragment has an enolform and makes up the pseudo aromatic system in the complex (Fig. 4). The signals of the β -ketoesterate ligand protons are shifted upfield by comparison with the free β ketoesters (Fig. 4). The signal of the methine group proton of the out planed ligands both in $PcZr(\beta-ketoester)_2$ and PcHf(β -ketoester)₂ is located near 3.35–4.40 ppm and in contrast to free β -ketoesters has more complicated aspects. Thus, instead of the expected singlet or doublet as in the case of asymmetric β-diketonato metallophthalocyanine complexes, we observe this signal as a multiplet or a doublet-doublet. The shift of proton signals of β-ketoester ligands depends on the influence of the individual phenyl fragment of the phthalocyanine, but not on π -electron conjugated macrocycle system as a whole, because the ligand plane and the phthalocyanine plane form an acute angle [7b]. In other words the protons of the axial coordinated B-ketoester ligands are in the cone of anisotropies of phenyl groups [18]. These spectroscopic properties have allowed us to conclude that two β -ketoester ligands are coordinated in

the *cis*-geometry about the central atom of the macrocycle as in the case of β -diketonato metallophthalocyanine complex [7b,15c]. The splitting of the signals of methine, methylene and methyl protons of the β -ketoester ligands points to the nonequivalence of these protons. This can be caused both by the formation of a mixture of *cis*- (A) and *trans*-(B) isomers of the substitutes in the axial fragments as by the awkward rotation of the bulky substitutes in the β ketoester ligands (Fig. 5).

3.3.2. Infrared spectra

The IR spectra of all synthesized complexes exhibit vibrational bands typical of the metallophthalocyanines [19]. The two moderately strong absorptions in the far-IR region at $350-250 \text{ cm}^{-1}$ assigned to the asymmetrical and symmetrical M-Cl modes, which are characteristic of starting compounds PcMCl₂, are absent. The bands near 1650-1500 cm⁻¹ which can be assigned to the v(C=O) and v(C=C) frequencies appear. This is an evidence for the existence of the conjugated system of the carbonyl C=O and ester COOR groups with a double carbon-carbon (C=C) bond which is typical of the enol form of β -ketonesters. That is to say the chelating rings with equivalent C-O and C-C bonds are formed. Absorptions due to the metal-oxygen vibration are located at 490-450 cm⁻¹ for all complexes. The presence of these absorption signals in the low-frequency region is the evidence of the formation of the pseudo aromatic ring [16]. Besides, vibrational bands being present at 3000 cm⁻¹. They can be relevant to vibrations of alkyl, or phenyl groups, that form a part of β -ketoesters as substitutes.

3.3.3. UV–Vis spectra

The electronic absorption spectra of the synthesized complexes show the typical patterns of phthalocyaninato metal complexes with the characteristic B and Q bands at 330–350 and 680–690 nm, respectively (Table 2) [7b,15c].



Fig. 4. ¹H NMR spectra of free isopropyl 3-oxobutanoato (a) and bis(isopropyl 3-oxobutanoato)zirconium (IV) phthalocyanine (b) in CDCl₃.

An insignificant bathochromic shift Q-band in the vis-spectra of $PcM(\beta$ -ketoeters)₂ compared with the position Q-band in the vis-spectra of $PcMCl_2$ is observed.

3.4. Cyclic voltammetry

The redox properties of PcMCl₂ and complexes **3–6** (Table 3) have been studied in 0.1 M Bu₄NBF₄ solution in CH₂Cl₂ at a Pt ultra micro electrode. On the cyclic voltammograms of the studied complexes, we observe two waves for each in the potential range from 270 to 1120 mV, and one wave at potentials from -1330 to

-990 mV (Table 3). The voltammograms of the zirconium (IV) and hafnium (IV) complexes with identical out planed ligands are practically identical (within 10–20 mV). The match between the curves for forward and backward scans suggests reversibility of the observed redox processes. The reversibility of the processes is also confirmed by the values of $\Delta E = E_{3/4} - E_{1/4}$ (the Tomes criterion), which are 58 mV [14] (Table 3). The differences between the $E_{1/2}$ potentials for the first oxidation wave and first reduction wave for all the studied β -diketoesterato phthalocyanine complexes of zirconium (IV) and hafnium (IV) are 1.5–1.7 V, which according to the literature data [1a] allows us to assign

Table 2 UV–Vis data for bis(β -ketoesterato)zirconium (IV) and hafnium (IV) phthalocyanines

Complex	λ , HM (log ε)				
	В	Satellite	Q		
1a	342.5 (4.78)	618.2 (4.58)	686.0 (5.29) w		
1b	340.5 (4.82)	616.9 (4.61)	684.3-685.8 (5.38) w		
2a	341.6 (4.75)	618.9 (4.42)	685.6–687.1 (5.16) w		
2b	340.1 (4.79)	616.5 (4.48)	684.6 (5.21) w		
3a	341.7 (4.85)	618.1 (4.52)	686.9 (5.27) w		
3b	339.5 (4.78)	616.2 (4.42)	684.1 (5.22) w		
4a	341.4 (5.10)	618.4 (4.70)	686.3 (5.45) w		
4b	340.8 (4.98)	616.9 (4.67)	685.2 (5.45) w		
5a	342.1 (4.71)	618.1 (4.37)	686.6 (5.07) w		
5b	341.0 (4.58)	616.9 (4.26)	684.4 (5.38) w		
6a	341.8 (4.63)	618.2 (4.29)	686.4 (5.00) w		
6b	342.8 (4.74)	616.9 (4.40)	684.9 (5.08) w		
7a	342.0 (4.72)	618.4 (4.45)	686.3 (5.21) w		
7b	340.4 (4.90)	616.7 (4.58)	684.8 (5.34) w		

 Table 3

 Oxidation and reduction potentials for the obtained complexes

N	$E_{1/2}$,V (ΔE)	$\Delta(E_{1/2}(\mathrm{ox}))$		
	1st oxidation	2nd oxidation	1st reduction	$-E_{1/2}(\text{red}), V)$
PcZrCl ₂	0.59			
PcHfCl ₂	0.60			
3a	0.42	0.98	-1.22	1.64
3b	0.44	0.99	-1.19	1.63
4a	0.47	1.04	-1.11	1.58
4b	0.48	1.04	-1.12	1.60
5a	0.61	1.12	-1.01	1.62
5b	0.62	1.14	-0.99	1.61
6a	0.27	0.98	-1.33	1.62
6b	0.28	0.97	-1.33	1.61
7a	0.51	1.10	-1.08	1.59
7b	0.53	1.11	-1.07	1.60

these waves to oxidation/reduction processes of the phthalocyanine ring. The absence of waves in the range between the potentials of halfwaves corresponding to oxidation/ reduction processes of the phthalocyanine ligand is an evidence that neither zirconium(IV) nor hafnium(IV) changes oxidation state in redox conversions of the complexes.

On the cyclic voltammograms of zirconium (IV) and hafnium (IV) dichlorophthalocyanines of composition PcMCl₂, when the scan is performed in the negative potential region, a single wave corresponding to the process [PcMCl₂]^{0/1+} is observed (Table 3). The wave is not reproduced from cycle to cycle, which may be due to electrode passivation. The substitution of the chloride ions by βdiketoesterate fragments in the studied mixed-ligand phthalocyanine complexes leads to a change in the electrochemical behavior of the entire system. The oxidation waves, which are indistinguishable for PcMCl₂, become pronounced for bis(β-diketoesterato)zirconium (or hafnium) phthalocyanine complexes, which can be explained by the redox activity of the chloride ions, on the one hand. On the other hand, the introduction of two β-ketoesterate fragments and the formation of quazi-aromatic rings of the



Fig. 5. The variants of coordination of the β-ketoester ligands one to another in the complexes: (a) *cis-cis*-geometry and (b) *cis-trans*-geometry.



Fig. 6. Cyclic voltammogram for bis(ethyl 3-oxo-3-phenylpropanoato)hafnium (IV) phthalocyanines in CH_2Cl_2 ; $1 - [PcHf(PhCOCHCOOEt)_2]^{1+/0}$, $2 - [PcHf(PhCOCHCOOEt)_2]^{2+/1+}$ and $3 - [PcHf(PhCOCHCOOEt)_2]^{1-/0}$.

central atom with β -ketoesters leads to the stabilization of electron π -conjugated system as a whole.

The phthalocyanine macrocycle is an 18-electron aromatic system for which the oxidation process can occur in two one-electron steps and the process of reduction can occur in four one-electron steps [1a]. Thus, the processes observed for the voltammograms obtained in Fig. 6 can be assigned to one-electron reversible processes and described by the following scheme:

$$[PcM(\beta-ketoester)_2]^{0/1-} \iff [PcM(\beta-ketoester)_2]^0 \iff [PcM(\beta-ketoester)_2]^{1+/0}$$
$$\iff [PcM(\beta-ketoester)_2]^{2+/1+}.$$

The presence of a phenyl group in β -ketoesterate ligands leads to the extension of the π -conjugated system as a whole which stabilizes the formation of the transition state – anion-radical and alleviates the processes of oxidation. The lengthening of the alkyl chain in β -ketoesterate ligands cumbers the processes of oxidation and alleviates the processes of reduction (Table 3).

4. Conclusions

The new mixed ligand bis(β -ketoesterato)zirconium (IV) and -hafnium(IV) phthalocyanine complexes have been synthesized by the reaction between PcMCl₂ (M-Zr, Hf) and free β -ketoesters. These has been determined by the data of elemental analysis, ¹H NMR, IR spectroscopy that two chlorine atoms are substituted for two β -ketoester fragments, which are coordinated in the cis configuration about the macrocycle plane. The X-ray crystallography data for bis(isopropyl 3-oxobutanoato)hafnium(IV) phthalocyanine confirm this geometry of the synthesized complexes. The central macrocycle of the phthalocyanine ligand is not exactly planar (deviations from the leastsquare plane exceed 0.15 Å) and has the conformation of an essentially flattened crown. The Hf(1) atom is 1.349(3)above this least-square plane. Cyclic voltammetry investigation shows that the introduction of two β -ketoester ligands to the central atom of phthalocyanine complex leads to both chemical and electrochemical stabilization of the whole Pc system. The presence of a phenyl group in β -ketoesterate ligands leads to the extension of the π conjugated system as a whole which stabilizes the forming of the transition state - anion-radical and alleviates the processes of oxidation. The lengthening of alkyl chain in β-ketoesterate ligands cumbers the processes of oxidation and alleviates the processes of reduction.

5. Supplementary data

Full crystallographic details have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for these materials should quote the full literature citation and reference number CCDC 611389.

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