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CHEMISTRY OF MACROCYCLIC AND METALLOCYCLIC COMPOUNDS

Synthesis and Reactivity of Zirconium and Hafnium Dihydroxophthalocyaninates

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Abstract—Two synthetic approaches for obtaining of zirconium and hafnium dihydroxophthalocyaninates (i.e. (a) that using the zirconium and hafnium alkoxides as the reactive precursors and (b) hydrolysis of zirconium and hafnium dichloridophthalocyaninates) were evaluated. Reactivity of zirconium and hafnium dihydroxophthalocyaninates in their exchange reactions with β-diketones and with decanoic acid was also studied; they were compared with those of zirconium and hafnium dichloridophthalocyaninates. The use of zirconium and hafnium dihydroxophthalocyaninates as the precursors in their reactions with acid-sensitive ligands, such as ketoesters, is found to be a more effective approach.

Keywords: zirconium complexes, hafnium complexes, phthalocyanines, axial ligands, exchange reactions

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INTRODUCTION

The high stability and wide range of optical and electrophysical properties of the zirconium and hafnium phthalocyanine complexes ($PcZrL_2$, $PcHfL_2$) [1–4], as well as the possibility of their modification through the coordinatively unsaturated central metal atom [5–11], makes them prospective for use as pigments and dyes, electrocatalysts [12], photoelectrocatalytic [13], electrochromic agents and other materials [14–17].

The main method of obtaining of zirconium and hafnium phthalocyaninates with non-planar ligands is the reaction of substitution of chlorine atoms in $PcMCl_2$ (M = Zr, Hf) with β-diketonate [5], β-ketoester [4], carboxylate ligands [9]. The peculiarity of such reaction is the release of hydrogen chloride, which can adversely affect the reaction pathway and thus on the formation of the target products. For example, hydrogen chloride could initiate the hydrolysis of acid-sensitive starting compounds, in particular, β-ketoesters, which in turn may lead to the formation of side-products and consequently to a decrease in the purity and yield of the target complexes. In similar reaction with phthalocyanine $PcM(OH)_2$ as starting compounds, their interaction with β-dicarbonyles or carboxylic acids generates water, which slightly affects either the starting materials or products of the reactions. Thus, $PcM(OH)_2$ are considered as the preferable starting compounds in ligand exchange reactions, but preparative methods for them have not been developed sufficiently and their reaction ability has been poorly studied. The purpose of this work is to optimize the $PcM(OH)_2$ preparation methods (Fig. 1) and study of their reactivity with β-diketones, β-ketoesters, and carboxylic acids.

EXPERIMENTAL

Zirconium and hafnium tetrachloride, *o*-phthalodinitrile, 1-phenyl-4,4,4-trifluoro-1,3-butanedione, dibenzoylmethane, ethyl acetoacetate, isopropyl

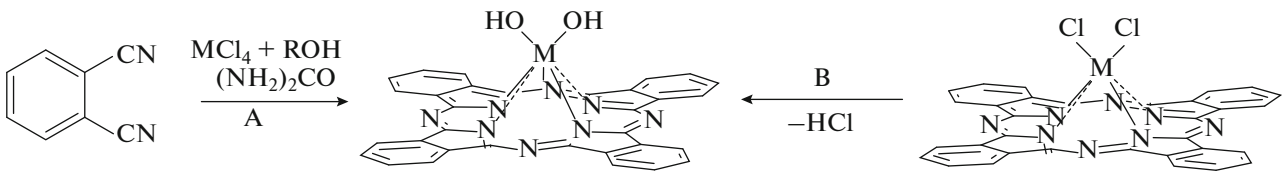


Fig. 1. Preparation of $PcM(OH)_2$ from metal alkoxides (A) and by hydrolysis of $PcMCl_2$ (B).

Table 1. Conditions for the synthesis of $PcM(OH)_2$ from metal alkoxides and by hydrolysis of the $PcMCl_2$

Synthesis from $M(OAlk)_4$					Hydrolysis of $PcMCl_2$			
metal	alcohol	*T*, °C	time, h	yield, %	reagent	*T*, °C	time, h	yield, %
Zr	$C_5H_{11}OH$	140	10	38	C_4H_9OH	120	8	0
	$C_7H_{15}OH$	180	8	40	NH_4OH	20	72	*
	$C_9H_{19}OH$	220	8	40	NH_4OH	95	12	88
Hf	$C_5H_{11}OH$	140	10	25	C_4H_9OH	120	8	0
	$C_7H_{15}OH$	180	8	27	NH_4OH	20	72	*
	$C_9H_{19}OH$	220	8	28	NH_4OH	95	12	76

* Partial hydrolysis.

3-oxobutanoate, (E)-1-ethoxy-3-oxo-3-phenylprop-1-en-1-olate, decanoic acid were purchased from Aldrich and used as received. Toluene, methanol, 1-butanole, 1-pentanol, 1-heptanol, 1-nonanol, aqueous ammonia solution, and all other organic solvents were of reagent grade and were used without further purification. Zirconium and hafnium dichloridophthalocyaninates were prepared by the reaction of MCl_4 with *o*-phthalodinitrile according to the published procedures [18].

^{1}H NMR spectra were recorded on a Varian VXR (400 or 300 MHz) spectrometer, TMS was used as internal standard, $CDCl_3$ was used as solvent.

The general method for synthesis of $PcM(OH)_2$ (M = Zr, Hf) in alcohol media. Zirconium or hafnium tetrachloride (0.012 mol) was mixed with the corresponding alcohol (20 mL) and heated to 100°C (HCl release was observed). Then phthalodinitrile (6.10 g, 0.048 mol) was added, after its dissolving urea (1.40 g, 0.023 mol) was added. The reaction mixture was heated to the boiling of the alcohol and kept for 8–10 hours. After cooling, the solution was filtered, the resulting precipitate was first washed with toluene and a small amount of methanol, and then within 4 hours was extracted with methanol in a Soxhlet apparatus from excess phthalodinitrile and products of metal tetrachloride hydrolysis. The resulting product was air-dried. The yields of the final products are shown in Table 1.

Synthesis of $PcZr(OH)_2$ and $PcHf(OH)_2$ by Hydrolysis of Corresponding $PcMCl_2$

$PcZr(OH)_2$. $PcZrCl_2$ (5 g, 0.007 mol) was suspended under stirring and heating with 25 mL of 25% aqueous ammonia solution. The mixture was kept at 95°C for 12 hours, cooled, filtered. The obtained precipitate was washed on the filter 3 times with 10 mL of water, then 3 times with the same amount of methanol, and 2 times with 5 mL of methyl-*tert*-butyl ether. The product was dried at room temperature for 24 hours. Yield, 4.15 g (88%).

$PcHf(OH)_2$. $PcHfCl_2$ (2.26 g, 0.003 mol) was suspended under stirring and heating with 10 ml of a 25% aqueous ammonia solution. The mixture was kept at 95°C for 6 hours, then 6 mL of ammonia solution was added and kept for 6 hours under the same conditions, then cooled and filtered. The precipitate was washed on the filter 3 times with 10 mL of water, then 3 times with the same amount of methanol and 2 times with 5 mL of methylene chloride. The product was dried at room temperature for 24 hours. Yield, 1.63 g (76%).

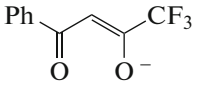
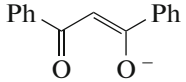
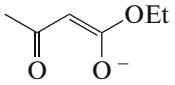
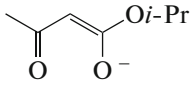
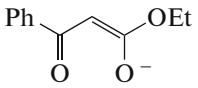
The general method for synthesis of $PcML_2$ (M = Zr, Hf; L = β-diketone, carboxylate). $PcM(OH)_2$ (0.4 mmol) was suspended in 10 mL of toluene, then 1.0 mmol of ligand was added and boiled for 2–5 hours. Next, the reaction mixture was filtered hot (T = 100–110°C), the solid residue was washed with hot toluene. The filtrate was cooled, the crystals formed overnight, filtered, washed with hexane and dried in vacuo at 100°C. The yields of the final products are shown in Table 2.

Bis(1-phenyl-4,4,4-trifluoro-1,3-butanedionato)zirconium(IV) phthalocyanine. ^{1}H NMR (400 MHz, chloroform-*d*), δ, ppm: 9.58–9.40 (m, 2H), 9.31 (dd, J = 7.6, 1.9 Hz, 2H), 9.15 (dd, J = 5.6, 3.0 Hz, 1H), 9.10 (d, J = 7.5 Hz, 1H), 8.92 (d, J = 7.3 Hz, 2H), 8.31–8.16 (m, 2H), 8.16–8.09 (m, 2H), 8.01 (tt, J = 7.3, 1.3 Hz, 2H), 7.97–7.87 (m, 2H), 7.47–7.34 (m, 2H), 7.14–6.98 (m, 4H), 6.85–6.76 (m, 1H), 6.76–6.69 (m, 3H), 5.15 (s, 2H).

Bis(1-phenyl-4,4,4-trifluoro-1,3-butanedionato)hafnium(IV) phthalocyanine. ^{1}H NMR (400 MHz, chloroform-*d*), δ, ppm: 9.54–9.43 (m, 2H), 9.31 (d, J = 7.5 Hz, 2H), 9.14 (dd, J = 5.6, 3.0 Hz, 1H), 9.09 (d, J = 7.5 Hz, 1H), 8.92 (d, J = 7.5 Hz, 2H), 8.19 (t, J = 7.2 Hz, 2H), 8.15–8.06 (m, 2H), 8.01 (t, J = 7.3 Hz, 2H), 7.95–7.87 (m, 2H), 7.45–7.32 (m, 2H), 7.11–6.96 (m, 4H), 6.75 (dd, J = 8.3, 1.1 Hz, 1H), 6.70 (dd, J = 8.3, 1.1 Hz, 3H), 5.08 (s, 2H).

Bis(dibenzoylmethanato)zirconium(IV) phthalocyanine. ^{1}H NMR (400 MHz, chloroform-*d*), δ, ppm: 9.37 (dd, J = 5.7, 3.0 Hz, 4H), 9.12 (dd, J = 5.5, 3.1 Hz, 4H), 8.29 (dd, J = 5.7, 2.9 Hz, 4H), 8.03 (dd, J =

Table 2. Reaction conditions and yields of $PcML_2$

Ligand	Original Pc	Time, h	Yield, %	Source
	$PcZrCl_2$	4	57	[5]
	$PcHfCl_2$	4	61	
	$PcZr(OH)_2$	5	77	
	$PcHf(OH)_2$	5	50	
	$PcZrCl_2$	5–6	70	[10]
	$PcHfCl_2$	5–6	75	
	$Zr(OH)_2$	5	53	
	$PcHf(OH)_2$	5	36	
	$PcZrCl_2$	6	39	[4]
	$PcHfCl_2$	6	37	
	$PcZr(OH)_2$	3	60	
	$PcHf(OH)_2$	3	46	
	$PcZrCl_2$	3–5	30	[4]
	$PcHfCl_2$	3–5	28	
	$PcZr(OH)_2$	5	85	
	$PcHf(OH)_2$	5	60	
	$PcZrCl_2$	3–5	25	[4]
	$PcHfCl_2$	3–5	25	
	$PcZr(OH)_2$	3	64	
	$PcHf(OH)_2$	3	45	
$C_9H_{19}COO^-$	$PcZrCl_2$	5	68	[9]
	$PcHfCl_2$	5	62	
	$PcZr(OH)_2$	2	63	
	$PcHf(OH)_2$	2	73	

5.8, 2.9 Hz, 4H), 7.46 (t, J = 7.3 Hz, 4H), 7.22 (t, J = 7.6 Hz, 8H), 7.06–6.99 (m, 8H), 5.71 (s, 2H).

Bis(dibenzoylmethanato)hafnium(IV) phthalocyanine. ^{1}H NMR (400 MHz, chloroform-*d*), δ, ppm: 9.28 (dd, J = 5.6, 3.0 Hz, 4H), 9.04 (dd, J = 5.6, 3.0 Hz, 4H), 8.21 (dd, J = 5.7, 2.9 Hz, 4H), 7.96 (dd, J = 5.7, 2.9 Hz, 4H), 7.45–7.32 (m, 4H), 7.16–7.05 (m, 8H), 6.97–6.89 (m, 8H), 5.58 (s, 2H).

Bis(ethyl 3-oxobutanoato)zirconium(IV) phthalocyanine (mix of *cis*- and *trans*-isomers). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.73–9.34 (m, 8H), 8.36–8.06 (m, 8H), 3.93–3.49 (m, 4H), 3.34–2.87 (m, 2H), 1.23 (s, 3H), 1.06 (s, 3H), 0.99 (t, J = 7.1 Hz, 3H), 0.88 (t, J = 7.1 Hz, 3H).

Bis(ethyl 3-oxobutanoato)hafnium(IV) phthalocyanine (mix of *cis*- and *trans*-isomers). ^{1}H NMR (300 MHz, chloroform-*d*), δ, ppm: 9.82–9.01 (m, 8H), 8.53–7.84 (m, 8H), 3.90–3.54 (m, 4H), 3.33–2.81 (m, 2H), 1.20 (s, 3H), 1.14–0.93 (m, 6H), 0.84 (t, J = 7.1 Hz, 3H).

Bis(isopropyl 3-oxobutanoato)zirconium(IV) phthalocyanine (mix of *cis*- and *trans*-isomers). ^{1}H NMR (400 MHz, chloroform-*d*), δ, ppm: 9.51–9.13 (m, 8H), 8.31–7.75 (m, 8H), 4.03 (p, J = 6.3 Hz, 1H), 3.86 (p, J = 6.3 Hz, 1H), 3.47 (s, 1H), 3.42 (s, 1H), 1.40 (d, J = 7.2 Hz, 3H), 1.19 (d, J = 6.3 Hz, 3H), 1.03 (s, 3H), 0.79 (s, 3H), 0.11 (d, J = 6.3 Hz, 3H), 0.01 (d, J = 6.1 Hz, 3H).

Bis(isopropyl 3-oxobutanoato)hafnium(IV) phthalocyanine (mix of *cis*- and *trans*- isomers). ^{1}H NMR (400 MHz, chloroform-*d*), δ, ppm: 9.48–9.16 (m, 8H), 8.15–7.82 (m, 8H), 4.02 (p, J = 6.2 Hz, 1H), 3.85 (p, J = 6.3 Hz, 1H), 3.50–3.36 (m, 2H), 1.52–1.38 (m, 3H), 1.20 (d, J = 6.4 Hz, 3H), 1.03 (s, 3H), 0.80 (s, 3H), 0.19–0.03 (m, 6H).

Bis(ethyl 3-oxo-3-phenylpropanoato)zirconium(IV) phthalocyanine (mix of *cis*- and *trans*-isomers). ^{1}H NMR (300 MHz, chloroform-*d*), δ, ppm: 9.54 (dd, J = 43.7, 7.3 Hz, 4H), 9.23 (dd, J = 52.1, 7.2 Hz, 4H), 8.45–8.21 (m, 4H), 8.13 (dt, J = 22.7,

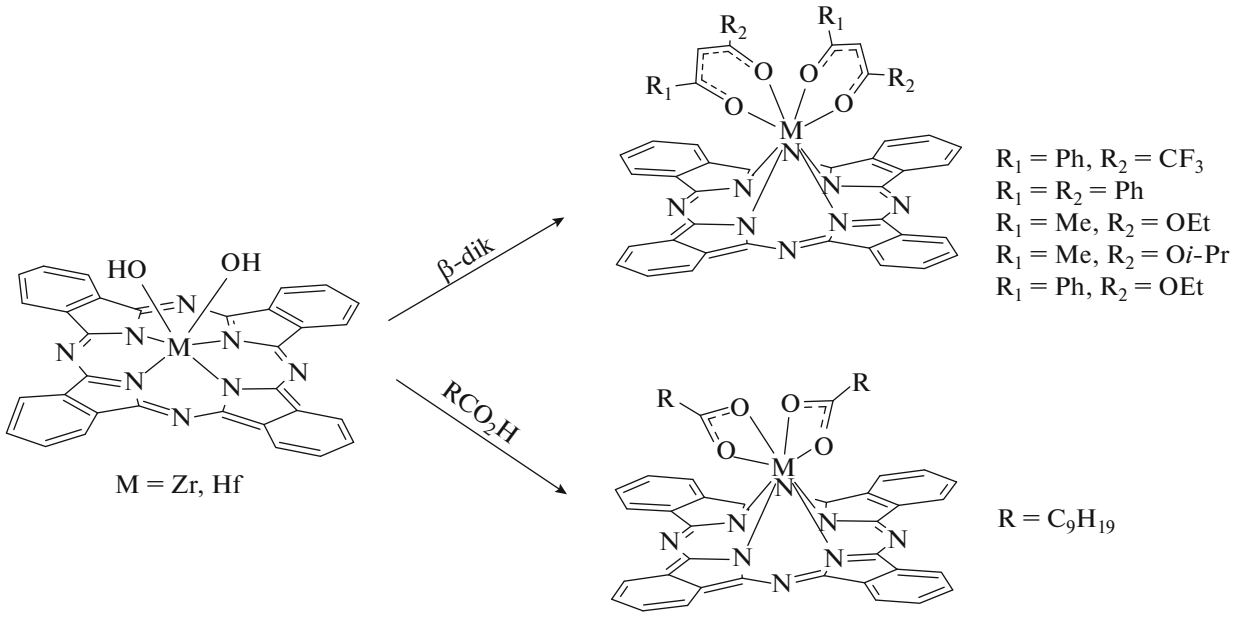


Fig. 2. Scheme of synthesis of $PcML_2$ from $PcM(OH)_2$.

7.0 Hz, 4H), 7.49–7.33 (m, 2H), 7.24–7.04 (m, 5H), 6.87–6.78 (m, 1H), 6.76–6.69 (m, 2H), 4.53–4.33 (m, 2H), 4.06–3.73 (m, 2H), 3.52–2.98 (m, 2H), 1.08 (t, J = 7.1 Hz, 3H), 1.01 (t, J = 7.1 Hz, 3H).

Bis(ethyl 3-oxo-3-phenylpropanoato)hafnium(IV) phthalocyanine (mix of *cis*- and *trans*-isomers). ^{1}H NMR (300 MHz, chloroform-*d*), δ, ppm: 9.55 (dd, J = 42.5, 7.2 Hz, 4H), 9.24 (dd, J = 50.8, 7.2 Hz, 4H), 8.53–8.02 (m, 8H), 7.58–7.31 (m, 2H), 7.25–7.05 (m, 5H), 6.83–6.74 (m, 1H), 6.77–6.67 (m, 2H), 4.46–4.30 (m, 2H), 3.98–3.70 (m, 2H), 3.42–2.90 (m, 2H), 1.07 (t, J = 7.1 Hz, 3H), 0.99 (t, J = 7.1 Hz, 3H).

Bis(decanoato)zirconium(IV) phthalocyanine. ^{1}H NMR (400 MHz, chloroform-*d*), δ, ppm: 9.20 (s, 8H), 8.02 (s, 8H), 1.19 (h, J = 6.4 Hz, 4H), 1.07 (dt, J = 13.8, 7.0 Hz, 4H), 0.97 (dt, J = 14.7, 6.9 Hz, 4H), 0.88–0.72 (m, 10H), 0.51 (p, J = 7.5 Hz, 4H), 0.42 (t, J = 7.5 Hz, 4H), 0.20 (p, J = 7.6 Hz, 4H), 0.00 (p, J = 7.6 Hz, 4H).

Bis(decanoato)hafnium(IV) phthalocyanine. ^{1}H NMR (400 MHz, chloroform-*d*), δ, ppm: 9.42–9.11 (m, 8H), 8.03 (dd, J = 5.8, 2.9 Hz, 8H), 1.12 (p, J = 6.5 Hz, 4H), 1.02 (dq, J = 9.3, 6.7 Hz, 4H), 0.92 (dt, J = 15.0, 6.9 Hz, 4H), 0.80–0.68 (m, 10H), 0.48 (p, J = 7.5 Hz, 4H), 0.40 (t, J = 7.6 Hz, 4H), 0.18 (p, J = 7.4 Hz, 4H), 0.00 (p, J = 7.5 Hz, 4H).

RESULTS AND DISCUSSION

One of the methods of synthesis of $PcM(OH)_2$ is the use of the corresponding metal tetrachlorides as starting compounds and high-boiling alcohols as solvents (Fig. 1, scheme A) [18, 19]. During the reaction, first, the metal alkoxide is formed and only after complete removal of the hydrogen chloride (release of hydrogen chloride as HCl evolution) it reacts with the phthalodinitrile. All reactions were carried out by boiling in high-boiling alcohols (T = 140–220°C) in the presence of urea since in [19] the possibility of formation of side-product non-metallic phthalocyanine in the absence of an ammonia donor is reported. According to the data in Table 1, the increase in the temperature of the reaction mixture slightly increases in the yields of the final products. The synthesis of $PcM(OH)_2$ by this method results in rather low yields, according to data of IR spectroscopy and elemental analysis on metal, purity of obtained complexes are quite low. In the case of performing this reaction without urea, or in the presence of pyridine instead of urea, it does not pass at all.

Another method of obtaining of $PcM(OH)_2$ is the hydrolysis of the corresponding $PcMCl_2$ (Fig. 1, scheme B). As noted in [20], $PcMCl_2$ are unstable and in the process of purification, they are hydrolyzed to products of the general formula $PcM(OH)_2$, where M = Zr, Hf. Here we have shown that $PcMCl_2$ are more hydrolytically stable than was considered by the authors in [20] and in our previous research [18]. Thus, the hydrolysis of $PcMCl_2$ did not occur upon boiling for 8 h in butanol saturated with water, and only partial hydrolysis was observed upon $PcMCl_2$ interaction with 10% aqueous ammonia upon stirring for 72 hours at room temperature. Partial hydrolysis was also observed when using water-pyridine or triethylamine systems. We have determined that boiling in 25% aqueous ammonia solution for 12 hours are the most effective conditions for hydrolysis of $PcMCl_2$ (Table 1).

The reactivity of the obtained $PcM(OH)_2$ was investigated in reactions with β-diketones and decanoic acid for ligands shown on the scheme in Fig. 2.

It was found that the reactivity of $PcM(OH)_2$ is generally similar to $PcMCl_2$ in their reactions with β-diketones (1-phenyl-4,4,4-trifluoro-1,3-butanedione, dibenzoylmethane) and decanoic acid (Table 2). However, in the reactions with β-ketoesters (ethyl 3-oxobutanoate, isopropyl 3-oxobutanoate, ethyl 3-oxo-3-phenylpropanoate), the yields of reactions with $PcM(OH)_2$ as the starting compounds were significantly higher than those with $PcMCl_2$. Such an increase in yields of $PcM(OH)_2$ reactions is suggested due to the absence of HCl release and consequently the absence of hydrolysis of the ketoester group.

CONCLUSION

Thus, it was found that the synthesis of $PcZr(OH)_2$ and $PcHf(OH)_2$ based on the corresponding alkoxides occurs with low yields (25–40%), and raising of the reaction temperature from 140 to 220°C increases the product yield insignificantly. It is shown that reaction of hydrolysis of $PcMCl_2$ passes effectively in more strict conditions (boiling in 25% aqueous ammonia solution for 12 hours) than reported earlier (boiling in pyridine with 5% of water or in water-alkaline isopropanol for 2 hours), use of such stricter conditions gives possibility to obtain $PcZr(OH)_2$ and $PcHf(OH)_2$ with high yields. For reactions with acid-sensitive β-ketoester ligands, the use of $PcZr(OH)_2$ and $PcHf(OH)_2$ as starting complexes provides higher yields and purity of the target products comparing to reaction starting from corresponding $PcMCl_2$.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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