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Preparation and characterization of aluminum phthalocyanine acetate, propionate, and benzoate

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ABSTRACT

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Keywords: Aluminum phthalocyanine carboxylate NMR MS Thermogravimetry Aluminum phthalocyanine acetate, propionate and benzoate were prepared by the reaction of hydroxy aluminum phthalocyanine and the corresponding acetic, propionic, and benzoic anhydrides. The reaction products were characterized by ¹H and ¹³C NMR spectroscopy and mass spectrometry. The thermal behavior of the products was determined by thermal analysis of particular samples. © 2012 Elsevier Ltd. All rights reserved.

Phthalocyanine compounds, mostly those of copper, are used both as dyestuffs and pigments. Derivatives of phthalocyanine have attracted considerable interest due to their growing potential as active materials in photosensitizers for photodynamic therapy,^{1,2} catalysts,³ active layers in photovoltaic panels,⁴ transistors,⁵ various sensors⁶ and light-emitting diodes.⁷ While the utility of the unsubstituted macrocycle of phthalocyanines is limited due to their very poor solubility in various solvents, substitutions at peripheral positions of the phthalocyanine macrocycle with appropriate functional groups improves their solubility and increases their effectiveness in many applications.

There are 16 peripheral positions on the phthalocyanine macrocycle which can be substituted either symmetrically or unsymmetrically. Besides peripheral positions, substitution of



Scheme 1.





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Table 1					
¹ H and ¹³ C NMR	chemical	shifts	of com	pounds	1-3

	1			2			3					
	$\delta_{\rm H}$	$\delta_{H}{}^{a}$	Δ^{b}	δ_{C}	$\delta_{\rm H}$	$\delta_{H}{}^{a}$	Δ^{b}	δ_{C}	$\delta_{\rm H}$	$\delta_{H}{}^{a}$	Δ^{b}	δ_{C}
1	_	-	_	150.8	_	_	_	150.9	_	_	_	150.9
2	_	_	_	136.9	_	_	_	137.0	_	_	_	136.9
3	9.66	-	_	123.3	9.66	_	_	123.4	9.68	_	_	123.4
4	8.47	-	_	130.9	8.47	_	_	130.9	8.47	_	_	131.0
COO	_	-	_	166.5	—	_	_	169.6	_	_	_	161.3
1′	-1.06	2.22	-3.28	21.1	-0.86	2.49	-3.35	27.5	_	_	_	133.2
2′	_	-	_	_	-1.33	1.18	-2.51	8.8	5.04	8.14	-3.10	126.5
3′	_	-	_	_	—	_	_	_	6.27	7.62	-1.35	126.5
4′	-	-	-	-	-	-	-	-	6.60	7.53	-0.93	129.6

The numbering of atoms is given in Scheme 1.

^a $\delta_{\rm H}$ in corresponding anhydride.

^b $\Delta = \delta_{\rm H}$ (in **1**, **2** or **3**) $-\delta_{\rm H}$ (in corresponding anhydride).



Figure 1. (a) APCI(–)-MS spectra of 1–3 in the *m*/*z* range 500–700 (b) MS/MS spectra of the molecular ions.

phthalocyanines can also be realized by the presence of axial ligands bound to the central metallic ion, located fully or partially in the cavity of phthalocyanine macrocycle.

Phthalocyanines with divalent metal ions are either planar systems or form structures with the central metal ion slightly above the phthalocyanine plane. The central atom is susceptible to nucleophilic axial binding.⁸ Such binding occurs through dative bonds. Phthalocyanines with trivalent and tetravalent metal ions form structures with one or two axially bound groups.

While there are several reports describing the synthesis and properties of various axially substituted phthalocyanines of silicon,⁹ titanium,¹⁰ tin,¹¹ gallium,¹² germanium,¹³ hafnium,¹⁴ and zirconium,¹⁴ very little has been published on axially substituted aluminum phthalocyanines. Aluminum phthalocyanine offers a wide range of applications due to its photosensitizing properties and usually contains a chloride or a hydroxy ligand on the central Al atom. The reactions of anhydrides of organic acids with axial hydroxy ligands bound to the central ion of aluminum phthalocyanine, targeting esters, have not been described previously.

Herein, we report the synthesis and characterization of aluminum phthalocyanines substituted with esters of acetic acid, propionic acid, and benzoic acid at the central aluminum ion. Aluminum phthalocyanine acetate (1),¹⁵ propionate (2),¹⁶ and benzoate (3)¹⁷ were prepared by the reaction of hydroxy aluminum phthalocyanine (HOAIPc) and the corresponding acetic, propionic, and benzoic anhydrides (Scheme 1). The isolated reaction products were characterized by ¹H and ¹³C NMR spectroscopy and by mass spectrometry. The thermal behavior of the products was determined by thermal analysis of particular samples.

In the ¹H NMR spectra,¹⁸ there were signals due to four equivalent 1,2-disubstituted aromatic rings of the phthalocyanine and those for the methyl, ethyl, and phenyl substituents. The relative integral ratios of these signals were 16:3 (CH₃) for compound **1**, 16:2 (CH₂) and 16:3 (CH₃) for compound **2** and 16:2 (*ortho*), 16:2 (*meta*) and 16:1 (*para*) for compound **3**. For proton chemical shifts, see Table 1. The ¹H chemical shifts of the carboxylate group protons were shifted considerably to lower frequencies compared to those in the starting anhydrides. This effect is caused by the existence of diamagnetic anisotropy. Ring-current effects lead to shielding or deshielding of the protons of the substituents depending on their mutual orientation with respect to the phthalocyanine plane. A very convincing and clear demonstration of this effect was

Table 2Weight losses for compounds 1–3

Compound	Weight loss for the first step (%)	Theoretical value (%)			
1	10.07	8.97			
2	12.89	11.92			
3	18.37	18.32			



Figure 2. TGA analysis of compound 3.

provided by Fernández and Fernándes-Sánchez¹⁹ for 1:2 complexes of iron(II) phthalocyanine with decylamine or benzylamine. The largest difference between proton chemical shifts in complexed and free amines (except for the concentration-dependent resonance position of the free amino group) was observed for protons of the first methylene group (about -5.7 ppm),¹⁹ while we observed a maximum difference of -3.35 ppm (Table 1). 2D gradient-selected (gs)-HMQC and gs-HMBC spectra¹⁸ were used for the assignment of ¹³C NMR resonances (Table 1).

Atmospheric pressure chemical ionization (APCI) mass spectra were recorded using an Agilent LC/MSD Trap XCT Plus mass spectrometer. Direct infusion of the sample solution in acetonitrile:dimethyl sulfoxide (5:1) into the APCI ion source was used. The AlPc derivatives were detected by APCI(–) MS (Fig. 1a). The radical molecular ions M^{--} were observed in particular cases at m/z 598, 612 and 660. The MS/MS experiment on these ions (Fig. 1b) clearly gave fragment ions of AlOHPc at m/z 557. Compound **3** also produced a fragment ion [M–44]⁻ (loss of CO₂) as the base peak. The fragment ions observed in the MS/MS spectra corresponded to the suggested structures.

Thermogravimetric analyses were performed using a Mettler Toledo TGA/DSC 1 STAR^e System in a 70 µl alumina crucible. A small amount of the test compound (\sim 5 mg) was weighed into the measuring crucible and heated using a controlled temperature program between 25 °C and 700 °C using a gradient of 10 °C/min. A flow of nitrogen (about 20 mL/min) was used as a protective gas. During the heating process weight-curves were recorded over the complete temperature range. All three compounds demonstrated the same behavior during the heating process. Cleavage of an acyl group occurred as the first step and aluminum phthalocyanine was formed. For compound **1**, only the first step was elimination of crystal water from the molecule with subsequent cleavage of an acyl group. Table 2 shows the weight losses during the heating of the studied samples. From the results it is apparent that the found values are in very good agreement with the theoretical values.

Figure 2 shows the weight-curve of compound **3**. The first loss of weight (18.37%) was observed between 190 °C and 480 °C. The second loss of weight (22.33%) was observed between 480 °C and 700 °C.

In conclusion, three axially substituted aluminum phthalocyanines containing acyl groups were prepared for the first time. All the compounds were fully characterized by ¹H and ¹³C NMR spectroscopy, mass spectrometry, and thermogravimetry. The products exhibit higher solubility in polar solvents and may be useful for several applications such as photodynamic therapy.

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- 15. Preparation of aluminum phthalocyanine acetate (1): 1 g of hydroxy aluminum phthalocyanine (HOAIPc) was dispersed in 50 mL of Ac₂O and the dispersion refluxed for 4 h. After cooling, the precipitated product was filtered, washed thoroughly with H₂O and dried in vacuo at 100 °C. Yield: 771 mg (72%).
- 16. Preparation of aluminum phthalocyanine propionate (2): 1 g of hydroxy aluminum phthalocyanine (HOAIPc) was dispersed in 50 mL of propionic anhydride and the dispersion refluxed for 4 h. After cooling, the precipitated product was filtered, washed thoroughly with acetone and dried in vacuo at 70 °C. Yield: 841 mg (76%).
- 17. Preparation of aluminum phthalocyanine benzoate (3): 1 g of hydroxy aluminum phthalocyanine (HOAIPc) was mixed with 25 g of benzoic anhydride and the mixture stirred and heated for 12 h at 200 °C. After cooling, the precipitated product was filtered, washed thoroughly with acetone and dried in vacuo at 70 °C. Yield: 609 mg (51%).
- 18. NMR spectra were recorded on a Bruker Avance II spectrometer (400.13 MHz for ¹H and 100.62 MHz for ¹³C) in DMSO-*d*₆. The ¹H and ¹³C chemical shifts were referenced to the central signal of the solvent [δ = 2.55 (¹H) and 39.6 (¹³C)]. 2D NMR experiments [gradient-selected (gs)-HMQC, gs-HMBC] were performed using TOPSPIN 2.1.
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