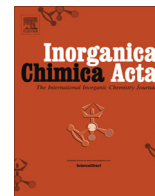




Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Expanding the family of substituted-at-core nickel(II) phthalocyanines

Yauhen Y. Karabach^a, Maximilian N. Kopylovich^{a,*}, Konstantin V. Luzyanin^{b,c},
M. Fátima C. Guedes da Silva^{a,*}, Vadim Yu. Kukushkin^b, Armando J.L. Pombeiro^{a,*}

^a Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

^b Institute of Chemistry, Saint Petersburg State University, Universitetsky Pr. 26, 198504 Stary Petergof, Russian Federation

^c Department of Chemistry, University of Liverpool, Crown Street, L69 7ZD Liverpool, United Kingdom

ARTICLE INFO

Article history:

Received 2 February 2016

Received in revised form 6 April 2016

Accepted 7 April 2016

Available online xxxxx

Keywords:

Nickel(II) complexes

Phthalocyanines

Solvothermal synthesis

Microwave-assisted reaction

ABSTRACT

A series of soluble in common organic solvents nickel(II) 14,28-dialkoxy-substituted phthalocyanines is synthesized by reaction of nickel acetate tetrahydrate with 1,2-dicyanobenzene in the presence of an alcohol under solvothermal conditions. Single crystal X-ray diffraction analyses reveal that the two alkoxy groups are added in a *syn*-conformation mode in all the studied cases. The use of microwave irradiation leads to decomposition of the nickel(II) 14,28-dialkoxy-substituted phthalocyanines.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The chemistry of metal-free (Pcs) and metallated (M-Pcs) phthalocyanines [1] has long been an area of active investigation, mainly due to the wide range of their applications in industry, laboratory and medicine, e.g. as dyes/pigments [2,3], light-harvesting molecular antennae for dye-sensitized solar cells [4–6], catalysts [7,8], nonlinear optical materials [9–11], organic semiconductors and electronic devices [12–16], active agents for phototherapy [17–19], chemical sensors [20], etc. In many of these applications a good solubility of Pcs and M-Pcs in different solvents is required [21–24]. However, typically phthalocyanines possess low solubility, mainly due to the formation of multiple π – π and other related intermolecular non-covalent interactions [25]. To weaken such interactions and at the same time to increase the non-covalent ones with molecules of solvents, various substituents can be introduced into the core or periphery of Pcs [21–24]. Thus, sulfo- or carboxy-groups allow to increase the solubility in polar solvents, in particular water [23], while alkoxy-substituents are useful to create lipophilic Pcs [8].

The introduced substituents also allow tuning of the other physical and chemical properties of Pcs species. For instance, the introduction of substituents at the Pc core gives rise to thermody-

namically unstable Pcs which easily decompose at heating or chemical treatment and thus can be used for thermal deposition of thin films and other functional materials [26,27]. Hence, modification of Pcs and M-Pcs by introduction of different substituents at various positions is an important task in the synthetic chemistry of phthalocyanines.

In some cases, the substituents can be introduced into the pre-prepared Pcs and M-Pcs, but their high robustness limits the post-modification. Moreover, although numerous examples of the peripheral modifications are known [1], Pc core (skeletal) modifications are much less exploited and usually are based on phthalonitrile treatment with lithium alkoxide [26,27] or solvothermal reactions of metal(II) acetate tetrahydrates with 1,2-dicyanobenzenes and some nucleophiles [28,29]. As a rule, the substituents can be introduced into positions 14 and 28 of the Pc core upon synthesis, in contrast to the post-synthetic modification.

Taking in mind the above considerations and following our interest in the synthesis of M-Pcs and related complexes [30–35], we decided to widen the scope of modified at core soluble Pcs species by the reaction between $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and phthalonitrile in different alcohols.

2. Results and discussions

Nickel(II) acetate tetrahydrate, phthalonitrile and several alcohols ROH (R = Me, Et, Prⁿ, Buⁿ and CH₂CH₂OME) were used as

* Corresponding authors.

E-mail addresses: kopylovich@yahoo.com (M.N. Kopylovich), fatima.guedes@tecnico.ulisboa.pt (M.F.C. Guedes da Silva), pombeiro@tecnico.ulisboa.pt (A.J.L. Pombeiro).

starting materials, the latter being applied as both reactants and solvents (Scheme 1, Table 1). In attempt to improve yields, two synthetic strategies with alternative energy inputs were applied: (i) solvothermal and (ii) microwave-assisted syntheses.

We started the study by modifying the known synthesis [28] and using methanol and ethanol as both reagents and solvents. We found that under optimized conditions the reaction of phthalonitrile and nickel(II) acetate tetrahydrate in methanol for 7 days at 70 °C and in ethanol for 4 days at 90 °C furnishes the corresponding M-Pcs **1** and **2** in 32% and 25% yields, correspondingly (Table 1). To expand the series, other aliphatic alcohols were employed under solvothermal conditions. Hence, the reaction in *n*-propanol, *n*-butanol or methoxyethanol for 7 days at 95 °C (for propanol) or 120 °C (for *n*-butanol and methoxyethanol) results in the formation of the corresponding 14,28-dialkoxy-substituted phthalocyanines **3**, **4** and **5** with 10%, 11% and 13% yields, respectively (Table 1).

In attempt to improve the synthetic procedure, we also performed a set of experiments under microwave irradiation: the metal source, dicyanobenzene and corresponding alcohol were mixed, sealed in a reactor and kept under MW irradiation for a certain time (Table 1). After that, the reaction mixtures were filtered and the residual solution was left for slow evaporation of the solvent to crystallize the product. Under microwave irradiation, the reaction in methanol (12 h at 80 °C) yielded the Ni-Pc **1** in only 2.3% yield. The reaction in *n*-propanol (9 h at 110 °C) resulted in the corresponding complex **3** in ca. 1% yield; also the formation of simple dark-blue non-substituted M-Pc was observed. When ethanol, *n*-butanol and methoxyethanol were used as solvents and reagents, we were unable to isolate reasonable amounts of the corresponding nickel(II) dialkoxy-substituted phthalocyanines. Hence, application of the microwave irradiation does not lead to any improvement of the synthetic procedure, possibly due to the destruction of the kinetic products (i.e., 14,28-dialkoxy-substituted Ni-Pcs).

Complexes **1–5** gave satisfactory C, H, and N elemental analyses that are consistent with the proposed formulations for the nickel

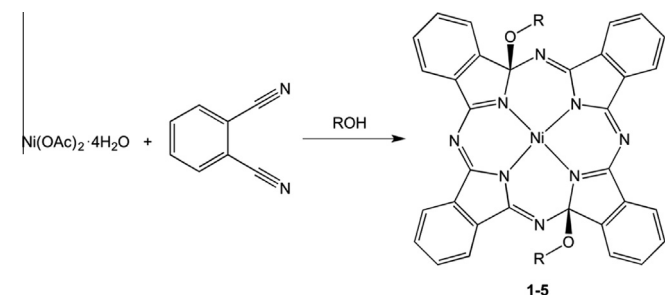
(II) dialkoxy substituted-at-core phthalocyanines. The ESI⁺-MS spectra of **1–5** display molecular ion peaks with the expected isotopic pattern (see Section 3). The IR spectra of **1–5** show no presence of the $\nu(\text{C}\equiv\text{N})$ stretching vibrations of the phthalonitrile $\text{C}\equiv\text{N}$ groups in the range between 2220 and 2198 cm^{-1} , but display strong bands due to $\nu(\text{C}=\text{N})$ of the products between 1650 and 1630 cm^{-1} . It also should be mentioned that Ni-Pcs **1** and **2** possess IR spectra identical to those previously published [28], and thus these compounds were not characterized in detail.

The Ni-Pcs **3–5**, as being new, were additionally characterized by NMR. In the ¹H NMR spectrum of **3**, the triplet at 3.82 ppm, multiplet at 1.79, triplet at 0.91, and multiplets at 7.95–7.52 ppm correspond to $-\text{OCH}_2\text{Et}$, $-\text{OCH}_2\text{CH}_2\text{Me}$, $-\text{OCH}_2\text{CH}_2\text{CH}_3$ and aromatic protons, respectively. Similarly, in the ¹H NMR spectrum of **4**, the triplet at 3.47 ppm, multiplet at 1.49, multiplet at 1.22, triplet at 0.90 and multiplets at 7.90–7.32 ppm correspond to $-\text{OCH}_2\text{Pr}^n$, $-\text{OCH}_2\text{CH}_2\text{Et}$, $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{Me}$, $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and aromatic protons, respectively. The ¹H NMR spectrum of **5** exhibits the aromatic protons at 7.86–7.42, while the $-\text{OCH}_2\text{CH}_2\text{O}-$ protons resonate at 3.64 and 3.55 ppm, and the methoxy protons at 3.20 ppm. The ¹³C(¹H) NMR spectra of complexes **3–5** display the sp² carbons of C=N within the range of ca. 168–165 ppm, the aryl carbons at ca. 142–117 ppm, while the sp³ carbon atoms within the distorted $[-\text{Ni}-\text{N}-\text{C}_{\text{sp}^2}=\text{N}-\text{C}_{\text{sp}^3}-\text{N}-]$ metallacycles appear at ca. 100–109 ppm (see Section 3). In addition, the structures of complexes **1**, **3** and **5** were elucidated by single crystal X-ray diffraction studies.¹

The crystal structures of **1**, **3** and **5** (Fig. 1) are composed of discrete monomeric units possessing distorted square-planar geometries (τ_4 values of 0.14–0.16) around the nickel centers [36]. The chelation of the Pc ligands through the N atoms [Ni–N bond distances in the 1.832(3)–1.8697(17) Å range] gives rise to two types of six-membered metallacycle rings, a planar $[-\text{Ni}-\text{N}-\text{C}_{\text{sp}^2}=\text{N}-\text{C}_{\text{sp}^2}-\text{N}-]$ [maximum deviations of 0.109(1)–0.141(1) Å, generally pertaining to the metal cation] and a distorted one $[-\text{Ni}-\text{N}-\text{C}_{\text{sp}^2}=\text{N}-\text{C}_{\text{sp}^3}-\text{N}-]$ [maximum deviations of 0.289(5)–0.336(3) Å pertaining to the out-of-plane sp³ carbon atom].

As a result of the *syn*-binding of the alkoxy groups to sp³ carbons in the structures of **1**, **3** and **5**, the molecules are highly bent. Analyzing the least-square planes of the four isoindole subunits in each molecule and the angles between them, one can consider these parameters as measures of deviations from planarity of the phthalocyanine ligand. While in complex **1** the rings are relatively displaced by a minimum value of 5.15° and a maximum of 37.21°, in complex **3** those values are of 7.85° and 47.97°, and in **5** they are of 15.41° and 46.40°. The overall increase of these angles in the order **1** < **3** < **5** may be related to the size of the alkoxy groups and stereochemical constraints. The minimum intermolecular metal···metal distances assume values of 7.764 (**1**), 7.685 (**3**) and 8.956 Å (**5**).

Apart from the above mentioned main structural details, molecules of **1** and **3** are involved in strong intermolecular $\pi\cdots\pi$ interactions connecting not only the phenyl groups of adjacent



Scheme 1. Synthesis of the 14,28-dialkoxy-substituted Ni-Pcs **1–5** [R = Me (**1**), Et (**2**), Prⁿ (**3**), Buⁿ (**4**), MeOCH₂CH₂ (**5**)]. The six-membered metallacycles of the inner core are planar $[-\text{Ni}-\text{N}=\text{C}_{\text{sp}^2}=\text{N}-\text{C}_{\text{sp}^2}-\text{N}-]$ and distorted $[-\text{Ni}-\text{N}-\text{C}_{\text{sp}^2}=\text{N}-\text{C}_{\text{sp}^3}-\text{N}-]$ (see also Fig. 1).

Table 1
Reaction conditions for the preparation of **1–5**.

ROH	Pcs	Solvothermal			Microwave-assisted		
		<i>t</i> (°C)	Time (d)	Yield (%)	<i>t</i> (°C)	Time (h)	Yield (%)
MeOH	1	70	7	32	80	12	2.3
EtOH	2	90	4	25	90	12	–
Pr ⁿ OH	3	95	7	10	110	9	1.1
Bu ⁿ OH	4	120	7	11	120	12	–
MeOCH ₂ CH ₂ OH	5	120	7	13	120	12	–

¹ Crystal data: **1**: C₃₄H₂₂N₈NiO₂, *M*, monoclinic, *a* = 22.9024(11), *b* = 9.706(5), *c* = 13.263(5) Å, α = 90.00°, β = 108.12(2)°, γ = 90.00°, *U* = 2802.0(18) Å³, *T* = 150(2) K, space group C2/c, *Z* = 4, *D*_{calc} = 1.501 g cm⁻³, μ (Mo K α) = 0.742 mm⁻¹, 13183 reflections measured, 3465 unique (*R*_{int} = 0.0505), *R*₁ = 0.0408, *wR*₂ = 0.0874, *R*₁ = 0.0652, *wR*₂ = 0.0941 (all data), GOF = 1.058. **3**: C₃₈H₃₀N₈NiO₂, *M* = 689.41, triclinic, *a* = 11.7822(13), *b* = 12.7756(12), *c* = 13.2010(13) Å, α = 88.281(6)°, β = 86.503(5)°, γ = 82.401(6)°, *U* = 1965.5(3) Å³, *T* = 150(2) K, space group P1, *Z* = 2, *D*_{calc} = 1.165 g cm⁻³, μ (Mo K α) = 0.534 mm⁻¹, 23098 reflections measured, 7124 unique (*R*_{int} = 0.0440), *R*₁ = 0.0525, *wR*₂ = 0.1506, *R*₁ = 0.0738, *wR*₂ = 0.1682 (all data), GOF = 1.038. **5**: C₃₈H₃₀N₈NiO₄, *M* = 721.41, monoclinic, *a* = 19.549(3), *b* = 16.578(3), *c* = 14.689(2) Å, α = 90.00°, β = 123.360(4)°, γ = 90.00°, *U* = 3976.1(11) Å³, *T* = 150(2) K, space group C2/c, *Z* = 4, *D*_{calc} = 1.205 g cm⁻³, μ (Mo K α) = 0.534 mm⁻¹, 8007 reflections measured, 3544 unique (*R*_{int} = 0.0706), *R*₁ = 0.0583, *wR*₂ = 0.1266, *R*₁ = 0.0902, *wR*₂ = 0.1387 (all data), GOF = 0.963.

Download English Version:

<https://daneshyari.com/en/article/5151962>

Download Persian Version:

<https://daneshyari.com/article/5151962>

[Daneshyari.com](https://daneshyari.com)