

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

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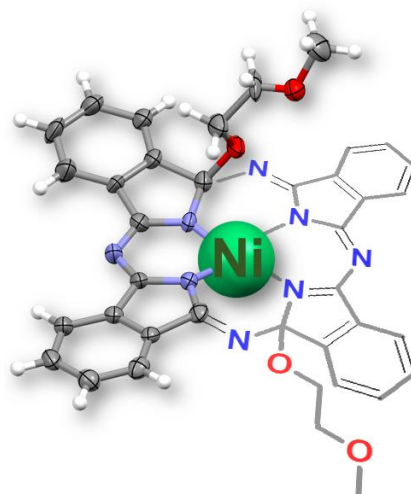
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Graphical Abstract



Two alkoxy groups are added in a *syn*-conformation mode in all the studied cases of nickel(II) 14,28-dialkoxy phthalocyanines.

Highlights

- ▶ Five unstable Ni(II) substituted-at-core 14,28-dialkoxy-phthalocyanines are easily synthesized by a solvothermal process
- ▶ Both alkoxy groups are added in a *syn*-mode
- ▶ Ni(II) dialkoxy-phthalocyanines are highly soluble in most common organic solvents

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.

Key words: Nickel(II) complexes, Phthalocyanines, Solvothermal synthesis, Microwave-assisted reaction.

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].

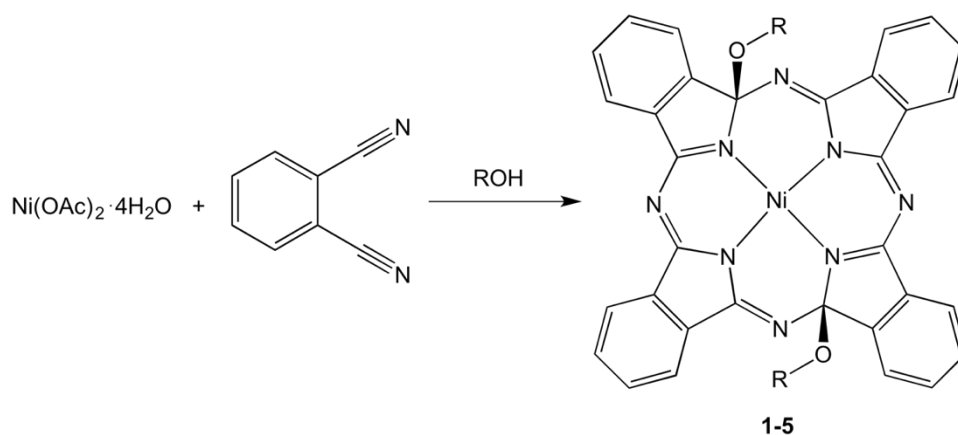
The introduced substituents also allow tuning of the other physical and chemical properties of Pcs species. For instance, the introduction of substituents at the Pc core give rise to thermodynamically unstable Pcs which easily decompose at heating or chemical treatment and thus can be used for thermal 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.

Results and Discussions

Nickel(II) acetate tetrahydrate, phthalonitrile and several alcohols ROH (R = Me, Et, Prⁿ, Buⁿ and CH₂CH₂OMe) were used as 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.



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 [-Ni-N=C_{sp2}-N=C_{sp2}-N-] and distorted [-Ni-N-C_{sp2}=N-C_{sp3}-N-] (see also Fig.1).

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

ROH	Pcs	Solvothermal			Microwave-assisted		
		t, °C	Time, d	Yield, %	t, °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	–

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 phthalocyaninates. 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 phthalocyaninates. The ESI⁺-MS spectra of **1-5** display molecular ion peaks with the expected isotopic pattern (see Experimental part). The IR spectra of **1-5** show no presence of the $\nu(\text{C}\equiv\text{N})$ stretching vibrations of the phthalonitrile C \equiv 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 -OCH₂Et, -OCH₂CH₂Me, -OCH₂CH₂CH₃ 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 -OCH₂Prⁿ, -OCH₂CH₂Et, -OCH₂CH₂CH₂Me, -OCH₂CH₂CH₂CH₃ and aromatic protons, respectively. The ¹H NMR spectrum of **5** exhibits the aromatic protons at 7.86-7.42, while the -OCH₂CH₂O- 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 sp^3 carbon atoms within the distorted $[-Ni-N-C_{sp^2}=N-C_{sp^3}-N-]$ metallacycles appear at *ca.* 100-109 ppm (see Experimental part). In addition, the structures of complexes **1**, **3** and **5** were elucidated by single crystal X-ray diffraction studies [36].

The crystal structures of **1**, **3** and **5** (Figure 1) are composed of discrete monomeric units possessing distorted square-planar geometries (τ_4 values of 0.14 – 0.16) around the nickel centres [37]. 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 $[-Ni-N-C_{sp^2}=N-C_{sp^2}-N-]$ [maximum deviations of 0.109(1) – 0.141(1) Å, generally pertaining to the metal cation] and a distorted one $[-Ni-N-C_{sp^2}=N-C_{sp^3}-N-]$ [maximum deviations of 0.289(5)– 0.336(3) Å pertaining to the out-of-plane sp^3 carbon atom].

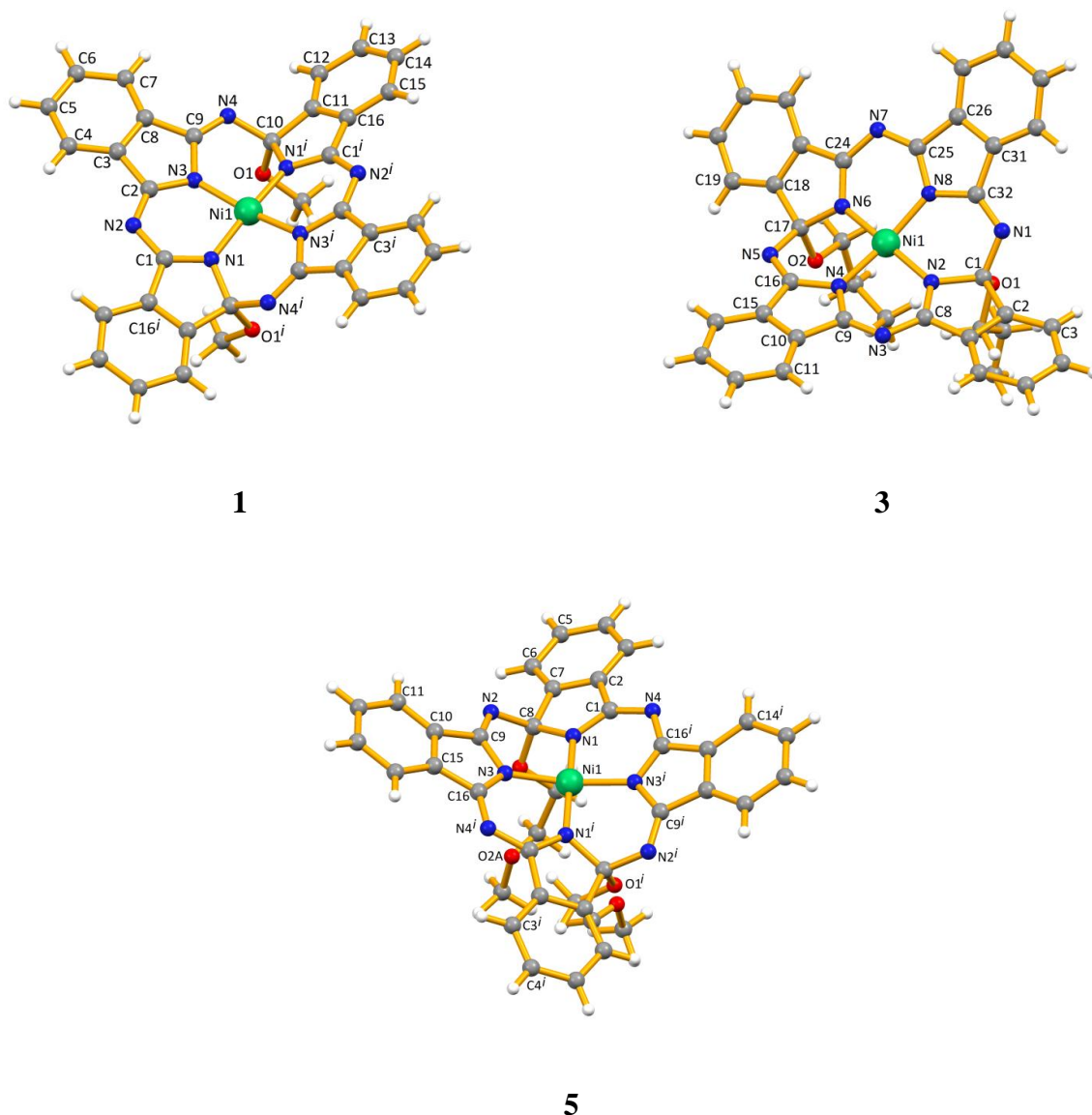


Figure 1. Molecular structures of complexes **1**, **3** and **5**. Symmetry codes to generate equivalent atoms: *i*) 1-x,y,1.5-z.

As a result of the *syn*-binding of the alkoxy groups to sp^3 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 phthalocyanide 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 molecules, but also a phenyl group of a molecule with the pyrrole ring of a vicinal one (Figures S1 and S2; most intense *centroid...centroid* distances below 3.800 Å). Known examples of other copper(II) and nickel(II) with 14,28-dialkoxy substituted phthalocyanate ligands [26,28] present similar conformations. Moreover, the geometry and bonding parameters within the Pc moieties of compound **1** agree with those reported [26,28].

Attempts to increase the yields of **1–5** by either running the reactions at higher temperatures or for a longer period of time result in the yield depletion and in many cases only simple unsubstituted phthalocyaninato nickel(II) complexes were formed. The small yields and instability of the isolated dialkoxy-substituted M-Pcs signifies that they are kinetic forms on the way to the thermodynamically stable highly symmetrical “simple” M-Pcs. Similarly, it was indicated that the 14,28-di-alkoxy-substituted Pc copper(II) complexes decompose under heating towards the corresponding copper(II) phthalocyanines [26]. It is very probable that the above mentioned strong intermolecular $\pi \cdots \pi$ interactions stabilize the kinetic intermediates **1–5** thus allowing their isolation and characterization.

In summary, we have isolated and fully characterized several new unstable nickel(II) phthalocyanines with alkoxy “at-core” substituents, derived from the convenient one-pot template condensation of phthalonitrile and alcohols on the nickel(II) matrix, performed under considerably mild conditions. The work deserves to be extended to a wider variety of alcohols with different electronic and steric features, and to other metals, towards the sustainable synthesis of a diversity of substituted-at-core phthalocyanines.

Experimental part

Materials and Methods. All chemicals were obtained from commercial sources and used as received. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. 1D (^1H , $^{13}\text{C}\{^1\text{H}\}$) NMR spectra were recorded on Bruker Avance II+ 300.13 (75.47 for ^{13}C) and 400.13 (100.61 for ^{13}C) MHz spectrometers at ambient temperature. The chemical shifts are reported in ppm using tetramethylsilane as the internal reference. Electrospray mass spectra (ESI-MS) were run with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 psi nebulizer pressure. Scanning was performed from m/z 100 to 1200 in methanol solution. The compounds were observed in the positive mode (capillary voltage = 80–105 V).

Solvothermal synthesis. Nickel(II) acetate tetrahydrate (55 mg, 0.221 mmol), 1,2-dicyanobenzene (100 mg, 0.781 mmol) and 3 mL of the corresponding alcohol (ROH) were combined and sealed in a stainless steel reactor and heated at 70 (**1**), 90 (**2**), 95 (**3**), 120 °C (**4** and **5**) for 4-7 days. Upon opening the reactor, a red solution and fine blue powder were observed. The blue powder was filtered off and was determined to be the unsubstituted “simple” phthalocyaninato nickel(II) complex by comparison of its IR spectrum to that of an authentic sample (Sigma) and also by the correspondence of its elemental analysis with the theoretical one. The eluate was cooled down and the formed colorless crystals were filtered off, while the resulting red solution was left for slow evaporation. Upon evaporation, red-orange crystalline blocks of Ni-Pc(OR)₂ were formed.

MW-assisted synthesis. Nickel(II) acetate tetrahydrate (55 mg, 0.221 mmol), 1,2-dicyanobenzene (100 mg, 0.781 mmol) and 3 mL of the corresponding alcohol were combined and heated in sealed reactor at 80 (**1**), 90 (**2**), 110 (**3**), and 120 °C (**4** and **5**) for 9-12 h under MW irradiation (Table 1). Upon opening the reactor, a red solution and traces of fine blue powder were observed. The blue powder was filtered off and was determined to be phthalocyaninato nickel(II) by comparison of its IR spectrum to that of an authentic sample (Sigma). The eluate was cooled down, and the formed colorless crystals were filtered off, while the resulting red solution was left for evaporation. Upon slow evaporation of the solutions, red orange blocks of **1** and **3** were formed.

[(**14,28**-(OMe)₂Pc)Ni] (**1**). Anal. Calcd for C₃₄H₂₂N₈NiO₂ (MW=633.28): C, 64.48; H, 3.50; N, 17.69. Found: C, 64.44; H, 3.90; N, 17.53%. ESI⁺-MS, m/z : 683 [M+H₂O+MeOH+H]⁺, m/z : 651

$[M+H_2O+H]^+$. IR spectra of this compound was found to be identical to that published [28]. The formulation of this compound was also proved by X-ray diffraction analysis.

[(14,28-(OEt)₂Pc)Ni] (2). Anal. Calcd for C₃₆H₂₆N₈NiO₂ (MW=661.34): C, 65.38; H, 3.96; N, 16.94. Found: C, 64.72; H, 3.94; N, 17.11%. ESI⁺-MS, *m/z*: 697 $[M+2H_2O+H]^+$, *m/z*: 679 $[M+H_2O+H]^+$. IR spectra of this compound is identical to that previously published [28].

[(14,28-(OPrⁿ)₂Pc)Ni] (3). Anal. Calcd for C₃₈H₃₀N₈NiO₂ (MW=689.39): C, 66.20; H, 4.39; N, 16.25. Found: C, 66.82; H, 4.68; N, 16.23%. ESI⁺-MS, *m/z*: 725 $[M+2H_2O+H]^+$, *m/z*: 707 $[M+H_2O+H]^+$. IR (KBr, selected bands, cm⁻¹): 3437(br), 3107 (m-w), 3080 (m-w), 3043 (m-w) ν (C–H from Ar); 2961 (m-w), 2924 (m-w) ν (C–H from CH₂ and/or CH₃); 1647 (m) ν (C=N); 1535(s), 1494(vs), 1412 (m), 1387 (m), 1199 (m), 1166 (m), 1144 (m), 1127 (m), 1095 (m), 1061 (s), 1043 (s), 1010 (s), 732 (s) δ (C–H from Ar). ¹H NMR (CDCl₃, δ): 7.95 (m, 7.0 Hz, 4H), 7.87 (m, 7.0 Hz, 4H), 7.62 (m, 6.0 Hz, 2H), 7.52 (t, 6.0 Hz, 6H), (Ar's), 3.82 (t, 7.5 Hz, 2H, OCH₂Et), 1.79 (m, 7.5 Hz, 4H, OCH₂CH₂Me), 0.91 (t, 7.5 Hz, 6H, OCH₂CH₂CH₃). ¹³C(¹H) NMR (CDCl₃, δ): 168.2 (C=N), 138.6, 138.4, 136.0, 132.7, 131.9, 130.0, 123.5, 122.5, 121.9 (carbons in Ar), 100.9 (NCO), 66.0 (OCH₂Et), 23.3 (OCH₂CH₂Me), 10.7 (OCH₂CH₂CH₃).

[(14,28-(OBuⁿ)₂Pc)Ni] (4). Anal. Calcd for C₄₀H₃₄N₈NiO₂ (MW=717.44): C, 66.96; H, 4.78; N, 15.62. Found: C, 67.00; H, 4.93; N, 15.47 %. ESI⁺-MS, *m/z*: 719 $[M+H]^+$. IR (KBr, selected bands, cm⁻¹): 3390 (br), 3122 (m-w), 3076 (m-w) ν (C–H from Ar); 2937 (m-w), 2901 (m-w) ν (C–H from CH₂ and/or CH₃); 1650 (m-w) ν (C=N); 1546 (s). ¹H NMR (CDCl₃, δ): 7.90 (d, 7.5 Hz, 4H), 7.70 (t, 6.0 Hz, 4H), 7.50 (t, 6.0 Hz, 6H), 7.32 (s, 2H), (Ar's), 3.47 (t, 7.0 Hz, 4H, OCH₂Prⁿ), 1.49 (m, 7.0 Hz, 4H, OCH₂CH₂Et), 1.22 (q, 7.0 Hz, 4H, OCH₂CH₂CH₂Me), 0.90 (t, 7.0 Hz, 6H, OCH₂CH₂CH₂CH₃). ¹³C(¹H) NMR (CDCl₃, δ): 167.5 (C=N), 142.2, 136.3, 135.5, 134.5, 134.0, 130.9, 128.9, 126.8, 123.0, 121.2, 118.1, 117.5 (carbons in Ar), 109.9 (NCO), 63.4 (OCH₂Prⁿ), 33.3 (OCH₂CH₂Et), 20.0 (OCH₂CH₂CH₂Me), 12.4 (OCH₂CH₂CH₂CH₃).

[(14,28-(OCH₂CH₂OCH₃)₂Pc)Ni]·(CH₃OCH₂CH₂OH) (5). Anal. Calcd for C₄₁H₃₈N₈NiO₆ (MW= 797.48): C, 61.75; H, 4.80; N, 14.05. Found: C, 62.94; H, 4.48; N, 15.55 %. ESI⁺-MS, *m/z*: 722 $[M - CH_3OCH_2CH_2OH + H]^+$. IR (KBr, selected bands, cm⁻¹): 3322 (br), 3096 (m-w), ν (C–H from Ar); 2922 (m-w) ν (C–H from CH₂ and/or CH₃); 1630 (m) ν (C=N); 1530(s). ¹H NMR (CDCl₃, δ): 7.86 (d, 7.5 Hz, 4H), 7.55 (t, 6.0 Hz, 4H), 7.50 (t, 6.0 Hz, 6H), 7.42 (s, 2H), (Ar's), 3.64 (t, 7.0 Hz, 2H, OCH₂), 3.55 (t, 7.0 Hz, 2H, OCH₂), 3.20 (s, 7.5 Hz, 6H, OCH₃). ¹³C(¹H) NMR (CDCl₃, δ): 165.0 (C=N), 140.4, 137.9, 136.4, 131.7 131.0, 129.1, 128.0, 119.3, 118.1 (carbons in Ar), 108.9 (NCO), 63.2 (OCH₂), 61.5 (OCH₂), 58.0 (OCH₃).

X-ray crystallography. X-ray diffraction data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-K radiation. Data were collected at 150 K using

omega scans of 0.5° per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART [38] software and refined using Bruker SAINT [38] on all the observed reflections. Absorption corrections were applied using SADABS [38]. Structures were solved by direct methods by using the SHELXS-97 package [39] and refined with SHELXL-2014 [40] with the WinGX graphical user interface [41]. The hydrogen atoms were inserted at geometrically calculated positions and included in the refinement using the riding-model approximation; Uiso(H) were defined as 1.2Ueq of the parent carbon atoms for phenyl and methylene residues and 1.5Ueq of the parent carbon atoms for the methyl groups. There were disordered molecules present in the structures of **3** and **5**. Since no obvious major site occupations were found for those molecules, it was not possible to model them. PLATON/SQUEEZE [42] was used to correct the data and potential void volumes of 505 (**3**) or 957 (**5**) Å³ were found worth of scattering (132 or 402 electrons per unit cells, in this order), thus featuring 26.3 or 24.1 % of the unit cell volumes, respectively. These were removed from the model and not included in the empirical formulas.

Appendix A. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication [CCDC 1451314 (**1**), 1451315 (**3**), and 1451316 (**5**)]. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>].

Acknowledgments

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- [36] 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-Kα) = 0.742 mm⁻¹, 13183 reflections measured, 3465 unique (R_{int} = 0.0505), R1 = 0.0408, wR2 = 0.0874, R1 = 0.0652, wR2 = 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 P-1, Z = 2, D_{calc} = 1.165 g cm⁻³, μ(Mo-Kα) = 0.534 mm⁻¹, 23098 reflections measured, 7124 unique (R_{int} = 0.0440), R1 = 0.0525, wR2 = 0.1506, R1 = 0.0738, wR2 = 0.1682 (all data), GOF = 1.038. **5**: C₄₁H₃₀N₈NiO₄, 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-Kα) = 0.534 mm⁻¹, 8007 reflections measured, 3544 unique (R_{int} = 0.0706), R1 = 0.0583, wR2 = 0.1266, R1 = 0.0902, wR2 = 0.1387 (all data), GOF = 0.963.
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