Synthesis and properties of new binuclear nickel(II) phthalocyanines

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New binuclear nickel(11) phthalonitrile complexes, *viz.*, Ni^{II} 2,2',9(10),9'(10'),17(18),17'(18'),24(25),24'(25')-tetra(phenylene-1,2-dioxy)bisphthalocyanine and Ni^{II} 2,2',9(10),9'(10'),17(18),17'(18'),24(25),24'(25')-tetra(4-*tert*-butylphenylene-1,2-dioxy)bisphthalocyanine, were synthesized. The complexes were characterized by electronic spectroscopy and MALDI—TOF mass spectrometry and studied as active components for membranes of ion-selective electrodes in solutions of dicarboxylic acids.

Key words: bisphthalodinitriles, binuclear nickel(11) phthalocyanines, MALDI–TOF mass spectrometry, electronic absorption spectra.

Porphyrins and their synthetic analogs, phthalocyanines, are under intense study as semiconductors, catalysts, and materials for nonlinear optics and liquid crystals. The porphyrin and phthalocyanine systems themselves have some useful properties. Nevertheless, much effort is directed to searching for more complicated related structures, *i.e.*, dimers and oligomers with different types of bridges, which possess unique spectral and electrochemical properties.¹⁻³ Since the porphyrin ring is relatively unstable in catalysis of multielectron processes,⁴ an important task is to synthesize and study thermally and photochemically more stable binuclear phthalocyanine complexes.

In this work, binuclear Ni^{II} phthanocyanines of the "ball" type conjugated through four pyrocatechol or 4-*tert*-butylpyrocatechol bridges were synthesized for the first time.

Results and Discussion

To synthesize the target products, we employed a procedure used earlier for the synthesis of some sandwichtype phthalocyanines and monophthalocyanines^{5,6} from the corresponding nitriles in the presence of a metal salt. This allows the stage of formation of isoindolines and metal-free phthalocyanines to be avoided.⁷

Based on 4-nitrophthalodinitrile (1) and pyrocatechol derivatives 2a,b, we synthesized 1,2-bis(3,4-dicyanophenoxy)benzene (3a) and 1,2-bis(3,4-dicyanophenoxy)-4-*tert*-butylbenzene (3b), whose tetramerization resulted in Ni^{II} 2,2['],9(10),9['](10[']),17(18),17['](18[']),24(25),24['](25['])-tetra(phenylene-1,2-dioxy)- (4a) and 2,2['],9(10),9['](10[']),

17(18),17'(18'),24(25),24'(25')-tetra(4-*tert*-butylphenylene-1,2-dioxy)bisphthalocyanines (**4b**) (Scheme 1).

It is known⁸ that non-substituted phthalocyanine complexes are poorly soluble in organic solvents and can be transferred in solution only on heating in α -chloronaphthalene, DMSO, or DMF. To enhance the solubility of the binuclear phthalocyanine, we synthesized complex **4b**, which is coupled through four pyrocatechol bridges with the Bu^t group in the benzene ring. However, the solubility of phthalocyanine complex **4b** turned out the same as that of complex **4a**.

High-molecular phthalocyanine-containing substances can be formed as by-products of the synthesis. This is indicated by both the insoluble portion of the reaction mixture and low yields of the target products. Nevertheless, repeated refluxing of the solid residue of the reaction mixture with CH_2Cl_2 makes it possible to extract almost completely the binuclear Ni^{II} phthalocyanines. Thus obtained complexes are highly soluble in lowboiling solvents, such as CH_2Cl_2 , $CHCl_3$, THF, and Me_2CO .

New binuclear Ni^{II} phthalocyanines of the "ball" type were chromatographed in a CHCl₃—EtOH system with the optimal ratio CHCl₃ : EtOH = 20 : 1. When only CHCl₃ or EtOH is used, the complexes are not eluted and, hence, we used EtOH for chromatographic removal of admixtures.

The electronic absorption spectra (EAS) of complexes 4a,b contain bands at 600-800 nm (Fig. 1) characteristic of phthalocyanines. The presence of the Bu^t group in the pyrocatechol bridge of complex 4b results in an insignificant bathochromic shift of the absorption maximum from 670 (4a) to 673 nm (4b).

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 $R = H(a), Bu^{t}(b)$

It is known^{9–11} that the EAS of planar binuclear phthalocyanines exhibit broadening or splitting of the Q band, which corresponds to electronic transitions between the π - π^* orbitals of the phthalocyanine rings, into two components. The total absorption intensity decreases compared to that of the monophthalocyanine analog. Such a behavior is explained^{9–11} by increased interaction between two phthalocyanine rings due to the bridges and, as a consequence, by a change in the π -conjugation mechanism. However, in our case, the general pattern of the



Fig. 1. Electronic absorption spectra of components 4a (1) and 4b (2) in CH₂Cl₂.

absorption spectra for complexes **4a**,**b** is similar to the spectral characteristic of metal monophthalocyanines. Probably, this is determined by two interacting π -phthalocyanine systems rigidly fixed above each other due to four bridges. This shifts the main maximum by 7 and 10 nm for complexes **4a**,**b**, respectively, compared to non-substituted Ni^{II} monophthalocyanines ($\lambda_{max} = 663$ nm).

The composition of binuclear Ni^{II} phthalocyanines of the "ball" type was confirmed by the MALDI—TOF* mass spectrometry. The m/z values in the mass spectra of compounds **4a,b** are 1574 and 1792, respectively, which corresponds (due to the isotopic splitting of the molecular ion peak and within the experimental error) to the calculated molecular weights of these complexes (1566.749 and 1791.174).

In our opinion, binuclear complexes **4a,b** can be used as receptors for selective binding of carboxylic dianions and ditopic compounds. It is schematically presented in Fig. 2.

Both reagents were studied as active components of anion-selective electrodes. Polyvinyl chloride membranes containing binuclear phthalocyanines plasticized with *o*-nitrophenyl octyl ether manifest an anionic response in

^{*} The method of matrix-activated laser desorption and ionization with a time-of-flight mass analyzer.



Fig. 2. Schematic structure of the complex formed between the binuclear phthalocyanine and ditopic molecule with several co-ordinate-active groups.

solutions of maleic and terephthalic acids against the background of tris(hydroxymethyl)aminomethane (pH \sim 7.8). However, to form the incomplete anionic function, a sensor needs prolonged conditioning in solutions of the potential-determining ion. In addition, to enhance the reproducibility of potential measurements, one has to introduce a cationogenic additive. The main reason for such a behavior of new reagents can be an insufficient structural correspondence of the reagent and analyte.

Probably, similar phthalocyanine structures but conjugated through different bridges from one side only can be more appropriate receptors. Due to the rotation around the bridge, binuclear phthalocyanine can exist in several conformations to provide great challenges for structural correspondence with the compound to be determined.

Thus, we synthesized for the first time Ni^{II} 2,2',9(10),9'(10'),17(18),17'(18'),24(25),24'(25')-tetra(phenylene-1,2-dioxy)- and 2,2',9(10),9'(10'),17(18), 17'(18'),24(25),24'(25')-tetra(4-*tert*-butylphenylene-1,2-dioxy)bisphthalocyanines by the tetramerization of the corresponding bisphthalodinitriles. The results obtained by the ionometric study indicate that the binuclear phthalocyanines can be used for selective binding and determination of carboxylic dianions and other ditopic compounds.

Experimental

Absorption spectra were recorded on a Helios- α spectrophotometer in the region from 190 to 1100 nm. ¹H NMR spectra were recorded on Bruker AM-300 and Bruker AC-200 instruments. The MALDI—TOF mass spectra were obtained on a Reflex III instrument in the reflection regime with a nitrogen laser (337 nm). 2,5-Dihydrobenzoic acid was used as matrix. Thin layer chromatography was carried out on Silufol UV-254 plates. All solvents and initial materials were purified immediately before use according to standard procedures.

4-Nitrophthalodinitrile (1). A vigorously stirred mixture of 4-nitrophthalodiamide (6.4 g, 78.4 mmol) and anhydrous Py (126 mL, 1.6 mol) was added dropwise for 2 h at 0-5 °C by POC1₃ (14.58 mL, 156.8 mmol). Then the temperature of the

reaction mixture was brought to ~20 °C, and the mixture was stirred for 2 h. The resulting suspension was poured into crushed ice (100 g), and the fine precipitate formed was filtered off and washed with ice-cold water to pH 7. The precipitate was dried on the filter at ~20 °C and then in a desiccator at 65 °C. After chromatography of the obtained substance (Al₂O₃ 5–40 mesh (Lachema), CHCl₃ as eluent) and evaporation of the solvent, product **1** was obtained as white crystals in 70% yield (9.47 g), m.p. 140–142 °C, R_f 0.33 (CHCl₃ as eluent).

4-tert-Butylpyrocatechol (2b) was synthesized from pyrocatechol and Bu¹OH using 85% phosphoric acid according to a previously described procedure¹² in 26% yield (m.p. 53 °C, b.p. 160 °C (22 Torr)).

1,2-Bis(3,4-dicyanophenoxy)benzene (3a). A mixture of 4-nitrophthalodinitrile (1) (2.12 g, 12.2 mmol), pyrocatechol (0.60 g, 5.4 mmol), and anhydrous K_2CO_3 (3.75 g, 27.0 mmol) in anhydrous DMF (14 mL) was stirred for 36 h at ~20 °C. After the end of the reaction, the mixture was poured into water (100 mL) and extracted with AcOEt (3×50 mL). The organic layer was washed with a saturated solution of K_2CO_3 $(3 \times 50 \text{ mL})$, 4 M HCl (~40 mL), water to the neutral reaction, and a saturated solution NaCl (100 mL) and dried above calcined Na₂SO₄. After chromatography on silica gel* (40/100 (Lachema), AcOEt-petroleum ether (3 : 5) as eluent) and evaporation of the solvent, product 3a was obtained as white needle-like crystals in 75% yield (1.47 g), m.p. 186 °C, Rf 0.29 (AcOEt-petroleum ether (3:5) as eluent). Found (%): C, 72.50; H, 2.26; N, 15.08. C₂₂H₁₀N₄O₂. Calculated (%): C, 72.92; H, 2.78; N, 15.46. ¹H NMR (CDCl₃), δ: 7.13 (dd, 2 H, H(12), $J_{\rm H(12),H(11)} = 8.6$ Hz, $J_{\rm H(12),H(8)} = 2.5$ Hz); 7.16 (d, 2 H, H(8), $J_{H(12),H(8)} = 2.5$ Hz); 7.41, 7.29 (both dd, 2 H each, H(3), H(4), H(5), H(6), $J_{H(3),H(4)} = J_{H(6),H(5)} = 6.1$ Hz, $J_{H(3),H(5)} = J_{H(6),H(4)} = 3.6$ Hz); 7.74 (d, 2 H, H(11), $J_{H(11),H(12)} = 8.6$ Hz). ¹³C NMR, δ: 109.6 (C(10)); 114.8, 115.2 (2 CŃ); 117.6 (C(9)); 120.7, 120.8 (C(4), C(5), C(3), C(6)); 123.6 (C(8)); 128.4 (C(12)); 135.5 (C(11)); 144.7 (C(1), C(2)); 160.4 (C(7)). MS (EI, 70 eV), m/z (I_{rel} (%)): 362 [M]⁺ (100).

1,2-Bis(3,4-dicyanophenoxy)-4-tert-butylbenzene (3b). A mixture of 4-nitrophthalodinitrile (1) (2.02 g, 11.7 mmol), 4*tert*-butylpyrocatechol (0.86 g, 5.2 mmol), and anhydrous K₂CO₃ (3.60 g, 26.0 mmol) in anhydrous DMF (13 mL) was stirred for 36 h at ~ 20 °C. After the end of the reaction, the mixture was poured into water (80 mL) and extracted with AcOEt (3×50) mL). The organic layer was washed with a saturated solution of K_2CO_3 (3×50 mL), 4 *M* HCl (~30 mL), water to the neutral reaction, and a saturated solution of NaCl (60 mL) and dried above calcined Na₂SO₄. After the solvent was evaporated, the brown oil was recrystallized from an AcOEt-petroleum ether mixture. Compound 3b was obtained as white needle-like crystals in 58% yield (1.25 g), m.p. 170-171 °C. Synthesis at a higher temperature (35-40 °C) did not shorten the reaction duration, however, the yield of the product increased to 68%. Found (%): C, 73.62; H, 4.15; N, 13.29. C₂₆H₁₈N₄O₂. Calculated (%): C, 73.63; H, 4.34; N, 13.39. ¹H NMR (CDCl₃), δ: 1.39 (s, 9 H, Me); 7.05–7.75 (m, 9 H, Ar). ¹³C NMR, δ: 31.3

^{*} The alternative method for purification is column chromatography on Al_2O_3 (5–40 mesh (Lachema)), CHCl₃ as eluent, column 50×5 cm. After the solvent was evaporated and the product was washed with hot hexane, the yield was 60%.

(C(Me₃)₃); 35.1 (<u>C</u>(Me)₃); 109.6, 114.9 (C(9), C(10), C(15), C(16)); 117.8 (C(6)); 120.5 (4 CN); 120.6, 120.7, 120.8 (C(5), C(3), C(12), C(18)); 123.0 (C(8), C(14)); 125.6 (C(11), C(17)); 135.5 (C(4)); 142.1 (C(2)); 144.1 (C(1)); 152.9 (C(7)); 150.7 (C(13)). MS (EI, 70 eV), m/z (I_{rel} (%)): 418 [M]⁺ (35), 403 [M - Me]⁺ (100).

2,2,9(10),9,(10),17(18),17,(18),24(25), Nickel(II) 24⁽²⁵⁾-tetra(phenylene-1,2-dioxy)bisphthalocyanine (4a). 1,2-Bis(3,4-dicyanophenoxy)benzene (3a) (0.95 g, 2.6 mmol) was dissolved on heating in isoamyl alcohol (15 mL), and $Ni(AcO)_2 \cdot 4H_2O$ (0.33 g, 1.3 mmol) and DBU (0.2 mL) were added to the mixture. The resulting mixture was refluxed for 5 h in an argon flow. Then the reaction mixture was cooled, and the insoluble precipitate was filtered off, thoroughly washed with petroleum ether, and dried in a desiccator for 3 h at 110 °C. According to the EAS and TLC data, the filtrate of the reaction mixture contained no phthalocyanine complexes. The target product was extracted by multiple boiling of the precipitate in CH_2Cl_2 . The yield was 0.097 g (9.5%), $R_f 0.25$ (CHCl₃-EtOH (20 : 1) as eluent). EAS, λ_{max}/nm : 670. MS MALDI-TOF, found, m/z: 1574 [M]⁺. $C_{88}H_{40}N_{16}O_8Ni_2$. Calculated: $M_r = 1566.749.$

Nickel(II) 2,2',9(10),9'(10'),17(18),17'(18'),24(25), 24'(25')-tetra(4-*tert*-butylphenylene-1,2-dioxy)bisphthalocyanine (4b) was synthesized similarly to compound 4a from 1,2-bis(3,4-dicyanophenoxy)-4-*tert*-butylbenzene (3b). The yield was 0.086 g (11%), $R_{\rm f}$ 0.28 (CHCl₃—EtOH (20 : 1) as eluent). EAS, $\lambda_{\rm max}$ /nm: 673. MS MALDI—TOF, found, m/z: 1792 [M]⁺, 1810 [M + H₂O]⁺. C₁₀₄H₇₂N₁₆O₈Ni₂. Calculated: M_r = 1791.174.

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