Metal Complexes of Phthalocyanine Structural Analogs with Oxygen- or Nitrogen-containing Heterorings. Synthesis and Properties

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Abstract — Nucleophilic substitution of the bromine atom and nitro group in 4-bromo-5-nitrophthalodinitrile and reduction of 4-benzoylamino-5-nitrophthalodinitrile gave, respectively, tribenzo[b,e,g][1,4]dioxocine-7,8-dicarbonitrile and 2-phenylbenzimidazole-5,6-dicarbonitrile. These compounds were used to synthesize new structural analogs of phthalocyanine, having oxygen- and nitrogen-containing heterorings, (tetratribenzo[b,e,g]-[1,4]dioxocino[7,8-b,g,l,q]-5,10,15,20-tetraazaporphyrinato)copper(II) and (23,73,123,173-tetraphenyl-tetrabenzimidazolo[5,6-b,g,l,q]-5,10,15,20-tetraazaporphyrinato)cobalt(II). Spectral properties of the resulting complexes were studied.

A large group of modified phthalocyanines (Pc) consists of their structural analogs in which the porphyrazine macroring is fused to various heterocycles. Despite extensive studies, such compounds have been explored to a much lesser extent, as compared to phthalocyanines. The available data suggest some prospects in their practical application [1–4]; therefore, further studies in this field are necessary, including those aimed at preparation of new derivatives. The present communication continues the series of our publications on the effect of functional substitution

on various physical and chemical properties of phthalocyanines [5–12]. It reports on the synthesis and properties of metal complexes derived from phthalocyanine structural analogs in which the peripheral benzene rings are fused to oxygen- or nitrogen-containing heterocycles, namely (tetra-tribenzo[b, e, g][1,4]dioxocino[7,8-b, g, l, q]-5,10,15,20-tetraazaporphyrinato)copper(II) (I) and (23,73,123, 173-tetraphenyl-tetra-benzimidazolo[5,6-b, g, l, q]-5,10,15,20-tetraazaporphyrinato)cobalt(II) (II).



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Electronic absorption spectra of (tetra-tribenzo[*b*,*e*,*g*][1,4]dioxocino[7,8-*b*,*g*,*l*,*q*]-5,10,15,20-tetraazaporphyrinato)copper(II) (I) ($c = 1 \times 10^{-5}$ M) in (*I*) DMF, (2) α -chloronaphthalene, and (3) H₂SO₄.

Copper complex I was synthesized by the "nitrile" technique in quinoline using tribenzo[b,e,g][1,4]dioxocine-7,8-dicarbonitrile (IV) as initial compound. 4-Bromo-5-nitrophthalodinitrile (III) is a unique synthon for the preparation of various substituted phthalodinitrile derivatives due to the presence of two groups which are very reactive toward nucleophiles. The bromine atom is usually replaced first [8–13]; however, conditions have been found under which nucleophilic substitution occurs simultaneously at the bromine atom and the nitro group [11–14]. Using 2,2'-dihydroxybiphenyl as nucleophile, we obtained tribenzo[b,e,g][1,4]dioxocine-7,8-dicarbonitrile (IV) which is necessary for the synthesis of compound I.



The complex was purified by reprecipitation from concentrated sulfuric acid, followed by Soxhlet extraction with methanol to remove impurities. (Tetratribenzo[b, e, g][1,4]dioxocino[7,8-b, g, l, q]-5,10,15,20-tetraazaporphyrinato)copper(II) (**I**) was isolated as a

dark green powder, which is insoluble in water and in dilute aqueous acids and alkalies and soluble in DMF, α -chloronaphthalene, chloroform, benzene, and acetone. It should be noted that solutions of **I** in DMF, chloroform, and benzene undergo coagulation with time (~20 min) and become colorless.

The electronic absorption spectrum of a freshly prepared solution of complex I in DMF contains bands with their maxima at λ 629 and 677 nm (see figure). The absorption bands are diffuse, indicating association of the solute. The spectral pattern does not change on replacement of DMF by benzene or chloroform. The spectral curves are typical of associates. In going to α -chloronaphthalene as solvent, the spectrum is transformed into a single-band one (see figure), indicating decomposition of the associates into monomeric species. Here, the first absorption band is displaced to the red region. The Q band appears at a longer wavelength, as compared to unsubstituted phthalocyanine, due to the presence of a dioxocine ring. As with other phthalocyanine metal complexes, replacement of the solvent by concentrated sulfuric acid induces a considerable red shift of the Q band as a result of protonation of the porphyrazine ring at the meso-nitrogen atoms.

Among structural analogs of phthalocyanine, compounds containing peripheral imidazole rings attract interest [2, 15, 16]. Unfortunately, only few published data are available on the synthesis and properties of such derivatives, presumably because of difficulties in the preparation of the corresponding precursors. It is known that benzimidazoles are formed by reduction and subsequent heterocyclization of acyl derivatives of *o*-amino nitro compounds [17]. By reduction of 4-benzoylamino-5-nitrophthalodinitrile (V) (which was synthesized by us previously [18]) with tin(II) chloride in concentrated hydrochloric acid we obtained for the first time 2-phenylbenzimidazole-5,6-dicarbonitrile (VII). The reduction was carried out at 70°C (reaction time 3 h). It involved intermediate formation of amine VI [17], which followed from the positive diazo test of the reaction mixture during the process. After 3 h, amino group was no longer detected, indicating completion of heterocyclization.

In the IR spectrum of compound **VII** we observed an absorption band at 2232 cm⁻¹ ($\nu_{C\equiv N}$), typical of the initial dinitrile, while no absorption bands corresponding to vibrations of nitro and carbonyl groups were present. A new absorption band appeared at 680 cm⁻¹, which is characteristic of a 4,5-disubstituted imidazole ring [19]. 2-Phenylbenzimidazole-5,6-dicarbonitrile (**VII**) is a light beige substance which,





unlike initial phthalodinitrile V, does not melt below 300°C. It is soluble in dilute alkali solutions, as well as in acetone, isopropyl alcohol, and dimethylform-amide.

Benzoylation of benzimidazoles according to Schotten–Baumann is known to result in cleavage of the imidazole ring and formation of dibenzoyl derivative of the corresponding *o*-phenylenediamine [17, 20]. By treatment of 2-phenylbenzimidazole-5,6-dicarbonitrile (**VII**) with benzoyl chloride in a dilute (1%) aqueous solution of sodium hydroxide we obtained 4,5-dibenzoylaminophthalodinitrile (**VIII**).



Compound **VIII** is readily soluble in organic solvents (such as acetone and isopropyl alcohol) but, unlike initial dinitrile **VII**, is insoluble in dilute aqueous alkalies and is characterized by a sharp melting point (232–234°C). The IR spectrum of **VIII** retains the C–N absorption typical of phthalodinitrile **VII** but lacks band in the region 680 cm⁻¹; in addition, a carbonyl absorption band appears at 1708 cm⁻¹. These data indicate opening of the imidazole ring.

Phthalodinitrile VIII can be used to prepare octa-4,5-benzoylaminophthalocyanines (see Experimental). Heating of 2-phenylbenzimidazol-5,6-dicarbonitrile with cobalt(II) chloride at 320–340°C afforded (23,73, 123,173-tetraphenyl-tetra-benzimidazolo[5,6-b,g,l,q]-5,10,15,20-tetraazaporphyrinato)cobalt(II) (II). Like compound I, complex II was purified by reprecipitation from concentrated sulfuric acid, followed by extraction with organic solvents to remove impurities. The product is readily soluble in DMF, DMSO, and concentrated sulfuric acid and insoluble in acetone, benzene, chloroform, and alcohols. Treatment of complex II with 20% oleum at 60–70°C gives the corresponding sulfonic acid which acquires solubility in aqueous ammonia or sodium hydroxide but is less soluble in DMF and DMSO, as compared to II.

Linear fusion of phenylimidazole fragments to the isoindole moieties of phthalocyanine molecule leads to a red shift of the *Q*-band (λ_{max} 714 nm, DMF), as compared to unsubstituted cobalt phthalocyaninate

 $(\lambda_{\text{max}} 660 \text{ nm}, \text{DMF})$. In going from DMF to concentrated sulfuric acid, a strong red shift of the Q band is observed $(\lambda_{\text{max}} 806 \text{ nm})$ due to protonation of the molecule. The basic centers in the latter may be not only phthalocyanine *meso*-nitrogen atoms but also nitrogen atoms of the imidazole rings.

EXPERIMENTAL

The electronic absorption spectra were recorded from solutions in organic solvents and concentrated sulfuric acid at room temperature using a Perkin–Elmer UV-Vis Lambda-20 spectrophotometer (λ range 300– 900 nm). The ¹H NMR spectrum of a 5% solution of compound **IV** in DMSO- d_6 (with TMS as internal reference) was recorded on a Bruker AC-200P instrument at the Institute of Organic Chemistry, Russian Academy of Sciences (Moscow, Russia).

Tribenzo[*b*,*e*,*g*][1,4]dioxocine-7,8-dicarbonitrile (IV). 2,2'-Dihydroxybiphenyl, 10 mmol, anhydrous potassium carbonate, 20 mmol, and 4-bromo-5-nitrophthalodinitrile, 10 mmol, were added under stirring to 30 ml of DMF. The mixture was stirred for 2 h at 90–100°C, cooled to room temperature, and poured into 100 ml of water. The precipitate was filtered off, washed with 50 ml of water, and recrystallized from DMF. Yield 79%, mp 205–206°C. ¹H NMR spectrum, δ , ppm: 8.15 s (2H, 1-H), 7.50–7.35 m (8H, 2-H, 3-H, 4-H, 5-H, J = 30 Hz). Found, %: C 77.28; H 3.39; N 8.94. C₂₀H₁₀N₂O₂. Calculated, %: C 77.41; H 3.25; N 9.03.

(Tetra-tribenzo[b,e,g][1,4]dioxocino[7,8-b,g,l,q]-5,10,15,20-tetraazaporphyrinato)copper(II) (I). Copper(I) chloride, 0.25 mmol, was added to a solution of 0.9 mmol of tribenzo[b,e,g][1,4]dioxocine-7,8dicarbonitrile in 10 ml of quinoline. The mixture was heated under vigorous stirring to the boiling point, stirred for 1.5 h at that temperature, cooled to room temperature, and poured into 50 ml of dilute (1:1)hydrochloric acid. The precipitate was filtered off, washed with water until neutral chloride ion-free washings, and dried at 60°C. The product was reprecipitated from concentrated sulfuric acid and extracted with methanol in a Soxhlet apparatus. Yield 25%. Electronic absorption spectrum, λ_{max} , nm: DMF: 676, 629; chloroform: 680; 612; benzne: 706, 674; αchloronaphthalene: 685, 654; conc. H₂SO₄: 822, 727.

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Found, %: C 60.9; H 3.0; N 7.9. $C_{80}H_{40}CuN_8O_8$. Calculated, %: C 59.1; H 2.5; N 6.9.

2-Phenylbenzimidazole-5,6-dicarbonitrile (VII). 4-Benzoylamino-5-nitrophthalodinitrile (V), 0.8 g, was added to a solution of 1.7 g of tin(II) chloride in 3 ml of concentrated hydrochloric acid. The mixture was heated to 70-75°C and was kept for 3 h at that temperature. Water, 15 ml, was then added, and the mixture was heated for 30 min on a boiling water bath. The precipitate was filtered off and washed with water until neutral washings. The crude product was dissolved in 1% aqueous sodium hydroxide, the solution was filtered off, and the filtrate was acidified with dilute hydrochloric acid. The precipitate was filtered off, washed with distilled water until neutral chloride ion-free washings, and dried at 110°C. Yield 0.5 g (76%). Found, %: C 73.2; H 3.1; N 22.5. C₁₅H₈N₄. Calculated, %: C 73.8; H 3.3; N 22.3.

4,5-Dibenzoylaminophthalodinitrile (VIII). Dinitrile **VII**, 2.0 g, was dissolved in 50 ml of 1% aqueous sodium hydroxide. The solution was cooled to $0-2^{\circ}$ C, 8 ml of benzoyl chloride and 290 ml of a 1% alkali solution were added in portions over a period of 1 h, and the mixture was kept for 3 h at that temperature. The precipitate was filtered off, washed with water and isopropyl alcohol, and dried at 50–60°C. Yield 1.2 g (40%), mp 232–234°C. Found, %: C 71.7; H 3.5; N 15.6. C₂₂H₁₄N₄O₂. Calculated, %: C 72.1; H 3.8; N 15.3.

(23,73,123,173-tetraphenyl-tetra-benzimidazolo-[5,6-*b*,*g*,*l*,*q*]-5,10,15,20-tetraazaporphyrinato)cobalt(II) (II). A mixture of 0.1 g of 2-phenylbenzimidazole-5,6-dicarbonitrile and 0.12 mmol of cobalt(II) chloride was heated to 320–330°C and kept until the melt solidified. The melt was cooled and washed with isopropyl alcohol, water, and acetone, and the product was reprecipitated from concentrated sulfuric acid. Yield 0.03 g (30%). Electronic absorption spectrum, λ_{max} , nm: 714 (DMF); 806 (conc. H₂SO₄). Found, %: C 69.1; H 2.9; Co 5.5; N 21.0. C₆₀H₂₂CoN₁₆. Calculated, %: C 69.6; H 3.1; Co 5.7; N 21.6.

[2,3,9,10,16,17,23,24-Octakis(benzoylamino)phthalocyaninato]cobalt(II). A mixture of 0.5 g of 4,5-dibenzoylaminophthalodinitrile (VIII), 0.06 g of cobalt(II) chloride, and 0.7 g of benzoic acid was heated to 180°C and kept for 45 min at that temperature. The melt was cooled and washed with isopropyl alcohol, water, and acetone, and the product was reprecipitated from concentrated sulfuric acid. Yield 0.2 g (30%). Electronic absorption spectrum, λ_{max} , nm: 708 (DMF); 809 (concd. H₂SO₄). Found, %: C 68.5; H 3.5; Co 3.7; N 14.8. C₈₈H₅₆CoN₁₆O₈. Calculated, %: C 69.3; H 3.7; Co 3.9; N 14.7.

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