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5-Bromotrimellitic Acid and Metal Phthalocyanines Based Thereon

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Abstract—5-Bromotrimellitic acid, its amide, and corresponding metal phthalocyanines on their basis were synthesized. The electronic absorption spectra of the latter are much affected by the nature of the complexing metal and the solvent.

Over the past years mixed-substituent phthalocyanines have received much study. They can be used as dyes, catalysts for redox processes, biologically active preparations, etc. [1, 2].

Of particular interest are phthalocyanines containing in the benzene rings carboxy groups together with other substituents. Carboxy-substituted phthalocyanines are characteristically readily soluble in aqueous media and polar organic solvents, which extends the field of their investigation and practical application.

At present ample information has been accumulated, concerning carboxy-substituted phthalocyanines with varied number and position of carboxy groups [3–5]. However, the information of mixed-substituent complexes containing carboxy groups together with other substituents is limited on account of the lack of reliable methods of their synthesis. Known methods [5] involve introduction of substituents into tetracarboxy-substituted metal phthalocyanines and are unsuitable for preparing complexes with preset number and position of new substituents. Therefore, to develop synthetic approaches to substituted trimellitic (4-carboxyphthalic) acids as starting materials for metal phthalocyanines is an urgent problem.

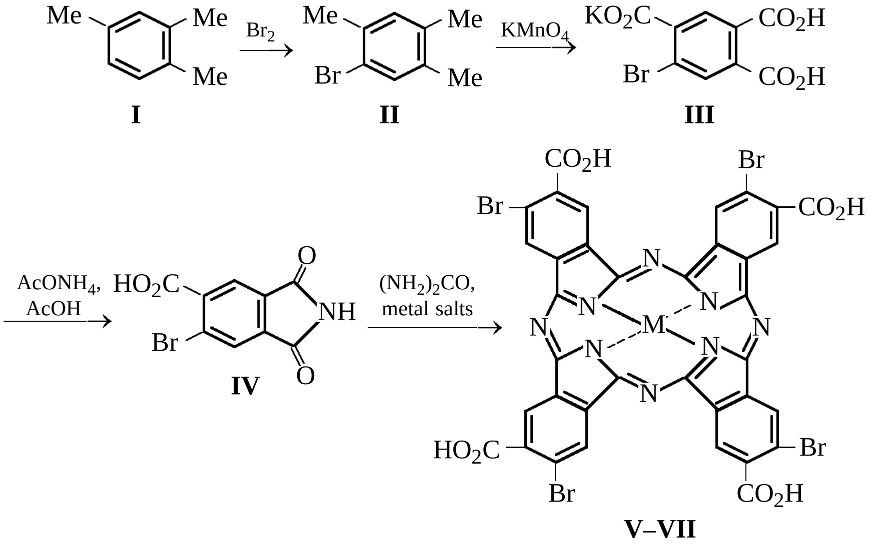
Here we report on the synthesis of 5-bromotrimellitic acid, its imide, and mixed-substituent metal phthalocyanines on their basis.

The starting compound, 1,2,4-trimethylbenzene (**I**), was brominated by the procedure in [6] in dry chloroform at 0–2°C. With account for the charge distribution on benzene carbon atoms in compound **I** and thermodynamic characteristics of formation of possible σ complexes on electrophilic substitution [7], bromination into the 5 position of the benzene ring to form 5-bromo1,2,4-trimethylbenzene (**II**) was substantiated. To prepare 5-bromotrimellitic acid (**III**), compound **II** was oxidized with potassium permanganate in aqueous alkali in the presence of pyridine, which allowed the reaction to be accomplished in a homogeneous medium and the reaction time to be much shortened. The precipitate of manganese dioxide was filtered off, and the filtrate was concentrated and acidified to precipitate compound **III** as colorless crystals. The product was filtered off and transformed in part into imide **IV** [8].

Compounds **III** and **IV** were identified by elemental analysis and IR spectroscopy. The IR spectra (Fig. 1) contain an absorption band at 670–680 cm^{-1}, formed by stretching vibrations of the C–Br bond, as well as a band of stretching vibrations of the C=O bond in the carboxy groups in aromatic dicarboxylic acids and their imides. Furthermore, the spectrum of compound **III** contains two bands (1350–1370 and 1610–1615 cm^{-1}) from stretching vibrations of bonds in the COO-group [9].

Bromo-and-carboxy-substituted metal phthalocyanines **V**–**VII** were synthesized by the “urea” method, specifically, by heating compound **III** or **IV** with urea, corresponding metal chlorides, acetates, or oxalates, and a catalytic amount of NH_4MoO_4. Complexes **V**–**VII** were isolated and purified by a scheme used in the synthesis of halo-and-sulfo-substituted phthalocyanines [10]. It should be noted that starting from compound **III** by the above procedure we could only prepare complex **V** (Co^{2+}). With imide **IV**, we could also prepare complexes **VI** and **VII** (Cu^{2+} and Fe^{2+}) and complex **V** in a higher yield than with acid **III**.

Metal complexes **V**–**VII** are dark blue powders with a violet shine. They are insoluble in water and low-polarity organic solvents, readily soluble in aqueous alkalis, and moderately soluble in DMF and



$M = Co^{2+}$ (**V**), Cu^{2+} (**VI**), Fe^{2+} (**VII**).

DMSO. They were identified by elemental analysis and IR and electronic absorption spectroscopy.

The IR spectra of complexes **V**–**VII** contain bands at 700–900 and 1050–1300 cm^{-1} characteristic of all metal phthalocyanines [11]. Like compounds **III** and **IV**, their derived metal phthalocyanines **V**–**VIII** show in the IR spectra a band at 675–680 cm^{-1} from stretching vibrations of the C–Br bond. The carbonyl absorption region changes radically in going from complexes **V**–**VII** to their ammonium and sodium salts. Thus, the spectra of complexes **V**–**VII** have a band at 1720–1730 cm^{-1} [ν(C=O)], whereas it the spectra of their ammonium salts this band is almost lacking and the above carboxylate C=O absorption at 1370-1375 and 1610–1620 cm^{-1} is prevailing (Fig. 1). Furthermore, in the 3300–3400 cm^{-1} region, there is a broad band characteristic of ammonium N–H bonds.

The electronic absorption spectra of complexes **V**–**VII** in aqueous alkalis and DMF (Fig. 2) show a strong *Q* band at 600–700 nm formed by π–π*-electron transitions in the main conjugation contour of the phthalocyanine macroring. The shape and position of this band are much dependent on the nature of the complexing metal and the solvent. Thus, the spectrum of complex **V** in 1% aqueous ammonia displays a narrow band (λ_{max} 682 nm) and a vibrational satellite (622 nm). The same complex in DMF gives a broad band with maxima at 676 and 636 nm.

The spectrum of complex **VI** is aqueous ammonia and DMF contains a broad band (λ_{max} 647–650 nm). The spectrum of complex **VII** in aqueous ammonia has a narrow band (λ_{max} 689 nm) with an ill-defined vibrational satellite; in going to DMF, the *Q* band gets broader and shifts blue by 13 nm.

The mentioned spectral changes, as follows from published data [12], can be related to the presence in the solutions either of free (complexes **V** and **VII** in 1% aqueous ammonia) or associated molecules (complex **VI**).

The band at λ_{max} 676 nm in the spectrum of complex **V** in DMF should be assigned to free molecules and that at λ_{max} 636 nm, to associates.

Comparing the electronic absorption spectra of the complexes, we can conclude that cobalt and iron complexes **V** and **VII** have a much weaker tendency for association than copper complex **VI**. This fact can be explained by the higher coordinating capacity of Co^{2+} and Fe^{2+} compared with Cu^{2+}. Compounds **V** and **VII** in aqueous and organic media (aprotic solvents) form extra complexes with solvent molecules or hydroxide ions as extra ligands, that are arranged axially (out of the phthalocyanine macroring plane) and hinder intermolecular interactions.

EXPERIMENTAL

The IR spectra in KBr were measured on an Avatar-360 FT–IR spectrophotometer in the range 500–4000 cm^{-1}. The electronic absorption spectra were taken in DMF and 1% aqueous ammonia on a Perkin–Elmer UV–Vis Lambda-200 instrument in the range 400–900 nm at 20°C for 10–5 M solutions.

5-Bromo-1,2,4-trimethylbenzene was synthesized by the procedure in [6], mp 44°C {published data: mp 44°C [6]}.

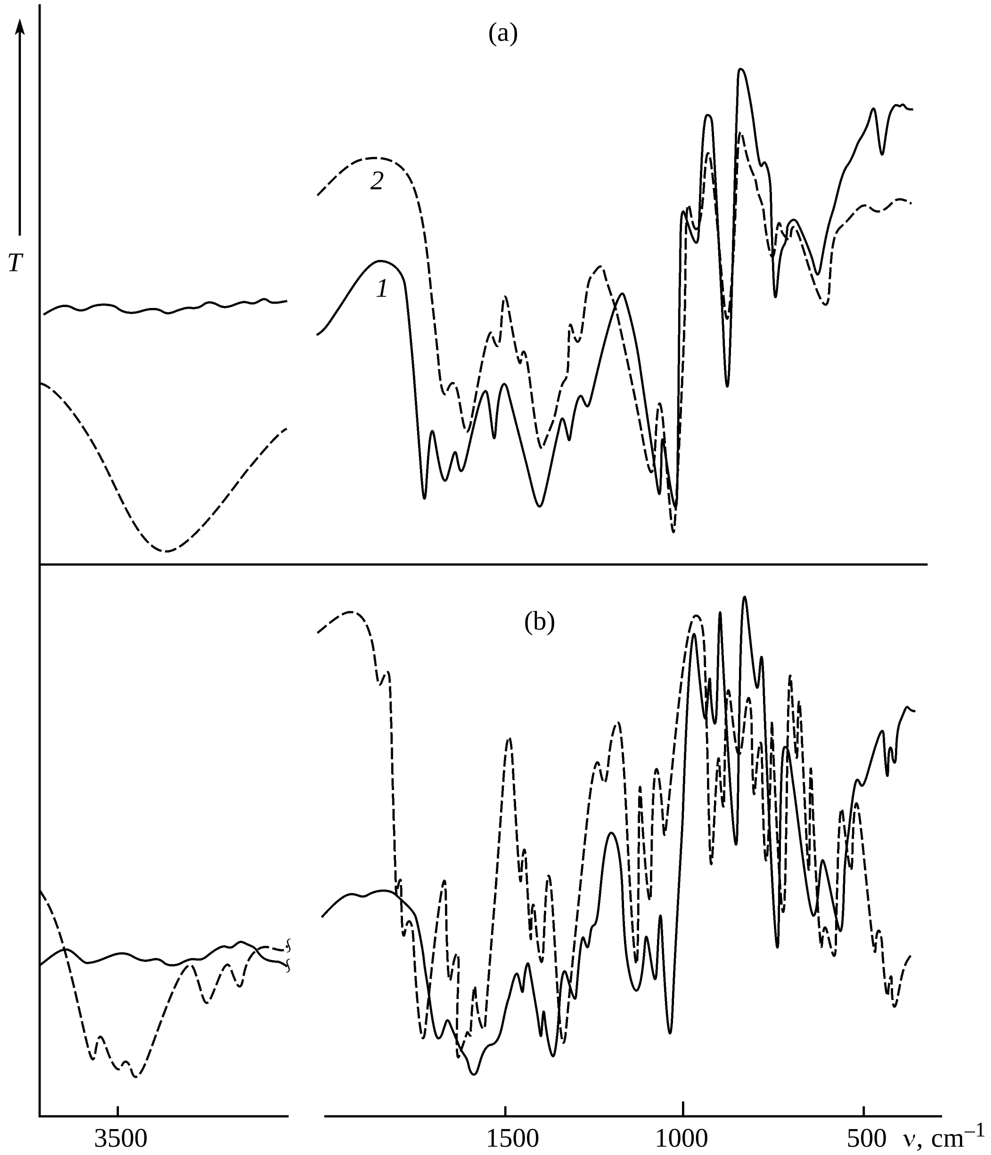


Fig. 1. IR spectra. (a): (*1*) Acid **III** and (*2*) imide **IV**. (b): (*1*) Complex **V** and (*2*) ammonium salt of complex **V**.

Potassium salt of 5-bromotrimellitic acid (III). Compound **II**, 0.1 mol, was suspended in 400 ml of water, the suspension was made weakly alkaline, and heated to 70°C, after which $KMnO_4$ was added to it with stirring in portions of 2.5 g. When three first portions had been added, the reaction mixture was heated to boiling and addition of $KMnO_4$ was continued until its crimson color no longer disappeared (test on filter paper). Excess $KMnO_4$ was reduced with ethanol. The suspension was filtered while hot and washed with hot water (2.50 ml). The filtrate and washings were combined, pyridine was removed by steam distillation until the distillate no longer smelled of pyridine. The residual solution was reduced by half and acidified to pH 4–5 with HCl. After cooling, a precipitate formed and dried at 80°C to constant weight to obtain 17 g (52%) of compound **III** as a colorless material soluble in water and aqueous alkalis, decomp. point 225°C. IR spectrum, ν, cm^{-1}: 680 (CBr), 1720 (C=O in CO_2H), 1611 and 1375 (CO in CO_2).

Imide of 5-bromotrimellitic acid (IV). Ammonium acetate, 0.07 mol, was added to 10 ml of glacial acetic acid. When the solved had dissolved completely, 0.01 mol of compound **III** was added. The reaction mixture was heated under reflux for 5 h, and 5 ml of acetic acid was distilled off. The residue was poured into 150 ml of saturated ammonium chloride. The precipitate that formed was filtered off, washed with

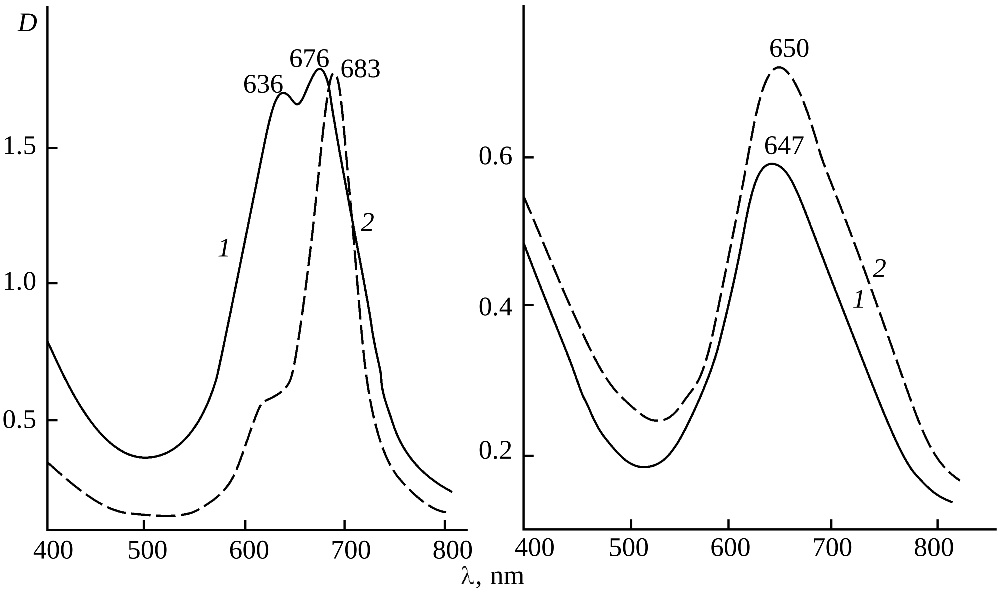


Fig. 2. Electronic absorption spectra. (a): Complex **V** in (*1*) DMF and (*2*) 1% aqueous ammonia. (b): Complex **VI** in (*1*) DMF and (*2*) 1% aqueous ammonia.

cold water to remove chloride ions, and dried at 80–90°C to constant weight to obtain 1.1 g (44%) of compound **IV** as a colorless powder, decomp. point 290°C. IR spectrum, ν, cm^{-1}: 680 (CBr), 1727 (C=O), 3400–3500 (NH). Found, %: C 39.7; H 1.1; Br 31.1; N 5.4. $C_9H_4BrNO_4$. Calculated, %: C 40.1; H 1.1; Br 29.7; N 5.2.

Cobalt(II) 2,9,16,23-tetrabromo-3,10,17,24-tetracarboxyphthalocyanine (V). *a*. A mixture of 1 mmol of compound **III**, 8 mmol of urea, 0.3 mmol of cobalt(2+) acetate, and a catalytic amount of ammonium molybdate was melted in the following temperature program: 140–150°C (90 min), 170–180°C (30 min), and 190–200°C (90 min). After cooling, the melt was thoroughly ground, mixed with 15% HCl, and heated at 70°C for 30 min. The precipitate was filtered off, washed with 10% HCl to colorless crystals washings and then with water to neutral and chloride-free washings. The solid material was dried, washed with methanol, and dried again to obtain 80 mg (30%) of compound **V**. IR spectrum, ν, cm^{-1}: 680 (CBr), 1720 (C=O). Found, %: C 40.7; H 1.1; Br 30.7; N 10.6. $C_{36}H_{12}Br_4CoN_8O_8$. Calculated, %: C 40.6; H 1.1; Br 30.1; N 10.5.

b. The procedure is similar to procedure *a*, except that compound **IV** was used as starting material instead of compound **III**, yield 130 mg (50%). IR spectrum, ν, cm^{-1}: 680 (CBr), 1720 (C=O). Electronic absorption spectrum, λ_{max}, nm: DMF: 676, 638; H_2O–NH_4OH (1%): 683, 622 sh. Found, %: C 40.6; H 1.2; Br 30.5; N 10.4. $C_{36}H_{12}Br_4CoN_8O_8$. Calculated, %: C 40.6; H 1.1; Br 30.1; N 10.5.

Copper(II) 2,9,16,23-tetrabromo-3,10,17,24-tetracarboxyphthalocyanine (VI) was prepared b y procedure *b*, using 1 mmol of compound **IV**, 8 mmol of urea, 0.3 mol of copper(I) chloride, and a catalytic amount of ammonium molybdate. Yield 114 mg (43%). IR spectrum, ν, cm–: 675 (CBr), 1720 (C=O). Electronic absorption spectrum, λ_{max}, nm: DMF 647; H_2O–NH_4OH (1%) 650. Found, %: C 39.9; H 1.1; Br 30.9; N 10.4. $C_{36}H_{12}Br_4CuN_8O_8$. Calculated, %: C 40.6; H 1.1; Br 30.1; N 10.5.

Iron(II) 2,9,16,23-tetrabromo-3,10,17,24-tetracarboxyphthalocyanine (VII) was synthesized in a similar way using 1 mmol of compound **IV**, 8 mmol of urea, 0.3 mmol of iron(II) oxalate, and a catalytic amount of ammonium molybdate. Yield 145 mg (58%). IR spectrum, ν, cm^{-1}: 675 (CBr), 1720 (C=O). Electronic absorption spectra, λ_{max}, nm: DMF: 676; H_2O–NH_4OH (1%) 689. Found, %: C 40.5; H 1.1; Br 30.9; N 10.4. $C_{36}H_{12}Br_4FeN_8O_8$. Calculated, %: C 40.8; H 1.1; Br 30.2; N 10.6.

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