Variations in the electronic absorption spectra of phthalocyanine films on successive treatment with nitrogen dioxide and ammonia

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The effect of alternating treatment of films of substituted metal phthalocyanines with nitrogen dioxide and ammonia on their spectral properties is discussed.

Key words: phthalocyanine derivatives, nitrogen dioxide, ammonia, complexes.

Interaction of thin sublimed films of metal phthalocyanines (MPc) with toxic gases is being intensely studied, due to the prospects of using these materials in chemical sensors[1—5] or as heterogeneous catalysts for the reduction of nitrogen dioxide with ammonia.[6] Moreover, data on the redox behavior of various MPc in solutions indicate that there are extensive possibilities of modifying their structures.[6—8] One of the main methods for studying the radical-anion and radical-cation states of MPc is electron spectroscopy (see, for example, Refs. 1, 5, 7—9). It has been shown that alternating treatment of sublimed MPc films with acceptor (NO_2, O_2, SO_2, *etc.*) and donor (NH_3, H_2, Li vapor, *etc.*) reagents in low concentrations induces an increase and decrease in the conductivity of the σ-layer,[1] respectively.

When we successively treated films of several MPc with nitrogen dioxide and ammonia at high partial pressures of NO_2 and NH_3 (p_i > 40 Torr), we did not observe such a clearly defined compensation effect, since the action of high NO_2 concentrations, as has been shown previously,[5] leads to the generation of radical mono-π-cations of MPc, which, in turn, substantially affects the conductivity of the MPc layer. This is accompanied by characteristic changes in the electronic spectra, and the present paper is devoted to discussion of these changes. A specified variation of the structure of elements of the phthalocyanine macromolecule is suggested as a method for affecting the phenomenon observed.

The methods used for the preparation of sublimed MPc films and for the measurements were similar to those reported in a number of previous papers.[3—5] Ph-thalocyanine derivatives were synthesized by previously described procedures.[6,7]

The absorption spectra of the initial CuPc and CoPc films as well as the spectra of these films treated with NO_2 and then with NH_3 are shown in Fig. 1, *a*. The initial dark-blue films become crimson-colored after treatment with nitrogen dioxide. This process[5] may be written as follows: $MPc - \bar{e} \rightarrow [MPc^{*}]^{+}$ (M = Cu, Co). At p_{NO_2} > 80 Torr, the CoPc films completely decolorize, and the spectrum corresponds to curve *4'* in Fig. 1, *a*. This is caused by further[8,9] oxidation: $[CoPc^{*}]^{+} - \bar{e} \rightarrow [Co^{3+}Pc^{*}]^{2+}$. After that, when ammonia is injected, the color of the MPc layer changes to light green (see curves *3* and *3'* in Fig. 1, *a*). A similar effect was observed when certain coordinating reagents, for example, pyridine, were added to a dichlorobenzene solution of $[CoPc^{*}]^{+}$ prepared by potentiostatic oxidation.[9] The adduct was colored light-green, which was explained by the formation of a low-spin octahedral complex in which pyridine is symmetrically coordinated to the Co atom. MPc containing extra ligands with an imino group are known;[8,9] at the same time, the ability of MPc to coordinate simple molecules (NH_3, H_2O, O_2) by the central metal atom has been thoroughly studied. The acceptor molecules like NO_2 are likely to interact with the periphery of the macroligand,[2,3] so that the metal atom retains its capability of coordinating donor molecules. Thus, we may assume that the following process occurs:

$$[MPc^{*}]^{+} + 2\,NH_3 \rightarrow [(NH_3)_2MPc^{*}]^{+}. \qquad (1)$$

The possible structure of the complex formed is presented in Fig. 1, *b*. The probability of the formation

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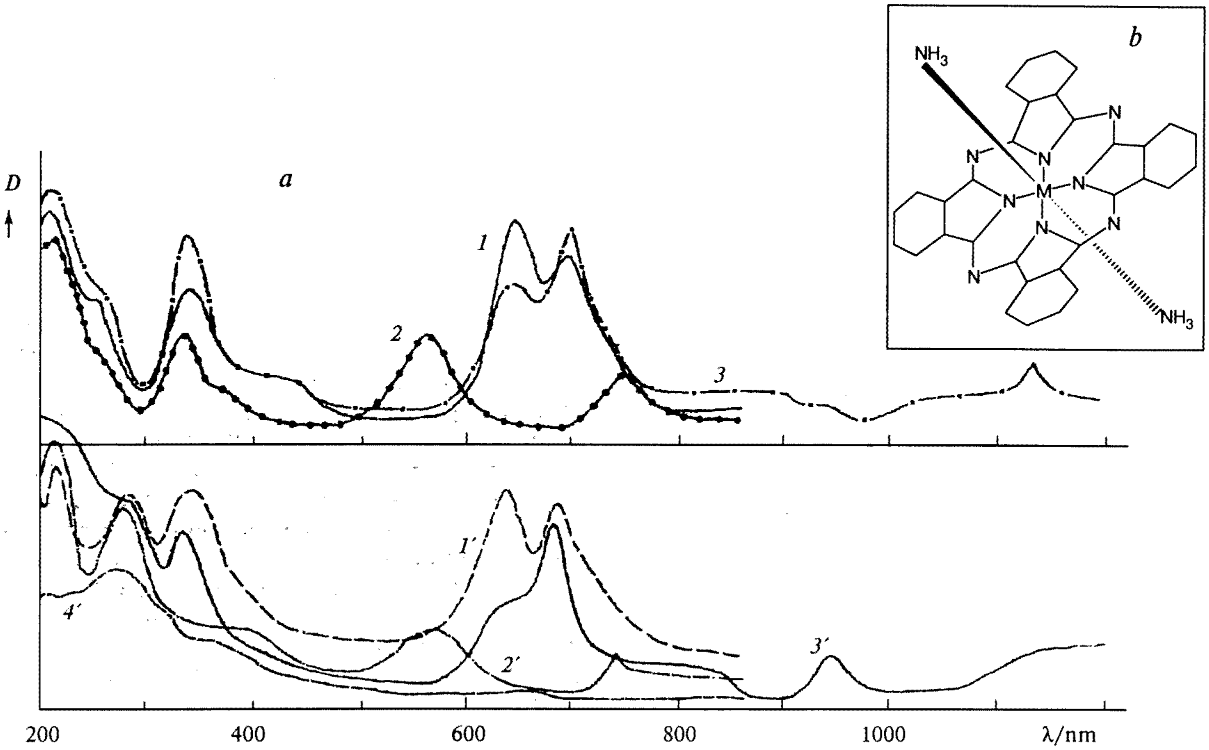

Fig. 1. *a*. Absorption spectra of copper phthalocyanine (*1—3*) and cobalt phthalocyanine (*1′—3′*) films in the initial state (*1, 1′*), after treatment with nitrogen dioxide (*2, 2′*), and after subsequent treatment with ammonia (*3, 3′*). Curve *4′* is the spectrum of the initial cobalt phthalocyanine film treated with nitrogen dioxide (p > 80 Torr). *b*. Schematic view of a metal phthalocyanine complex with two ammonia extra ligands.

of the product and its stability, as shown below, depend substantially on the structure of the MPc molecule.

The $[(NH_3)_2CoPc^*]^+$ complex (see Fig. 1, *a*, curve *3′*) is the most stable: its prolonged storage in air does not lead to any variations in its spectrum. Previously it has been noted that cobalt complexes exhibit high catalytic activities in the reduction of nitrogen oxides with ammonia.[6] In the present case, as in the case of the $[(NH_3)_2CuPc^*]^+$ complex, we observed weak absorption in the near IR region, at ~930, >1500, and ~1100 nm (see Fig. 1, *a*, curves *3* and *3′*). It is of interest that the initial CuPc films treated with ammonia exhibited no substantial absorption in the near IR region.[4] Therefore, the long-wave bands expected for a charge-transfer complex appear only in those cases where NH_3 coordinates to the previously generated radical-cation form of MPc. The initial spectral pattern of the CoPc film is restored (see Fig. 1, *a*, curve *1′*) only after the film is kept at 100—120 °C for 15 min. The CuPc films spontaneously return to the initial state over a period of 24—36 h.

We also studied films of copper and cobalt 4,4″-dichlorophthalocyanines ($CuPcCl_2$ and $CoPcCl_2$), which are characterized by a reduced symmetry of the macroligand. It was found that these structural changes have no effect on the transformations observed.

Successive treatment of cobalt 4,4′,4″,4‴-tetrabromophthalocyanine $CoPcBr_4$ (Fig. 2, curves *1—3*) with NO_2 and NH_3 also yields a stable complex, whose spectrum is similar to that of $[(NH_3)_2CoPc^*]^+$ and resembles the spectra of extra-doped tetrahalo-substituted phthalocyanines[7] (see Fig. 2, curve *2*). However, the initial spectrum of the film is not restored after heat treatment (see Fig. 2, curve *3*); for example, the Davydov splitting of the Q-band is completely absent, which indicates that the ordered crystal structure of the layer has been destroyed through the action of the gases.

Copper 4,4′,4″,4‴-tetrabromophthalocyanine $CuPcBr_4$ forms an unstable complex, $[(NH_3)_2CuPc^*Br_4]^+$ (with a lifetime of 5—10 s), which is probably caused by the increase in the ionization potential of the phthalocyanine ligand due to the introduction of four electronegative halogen atoms.

Metal-free phthalocyanine containing no metal is transformed into a radical mono-π-cation state on treatment with nitrogen dioxide by releasing an electron from the π-system of the macroring, as indicated by the absorption spectra, and its sublimed film acquires a specific crimson color. After the subsequent treatment with ammonia or heat treatment the initial spectrum of the film is restored, no intermediate products being observed. This is consistent with the scheme suggested for reaction (1), *viz.*, NO_2 molecules react with the π-system at the periphery of the ligand, and NH_3 is coordinated to the metal atom of the MPc molecule,

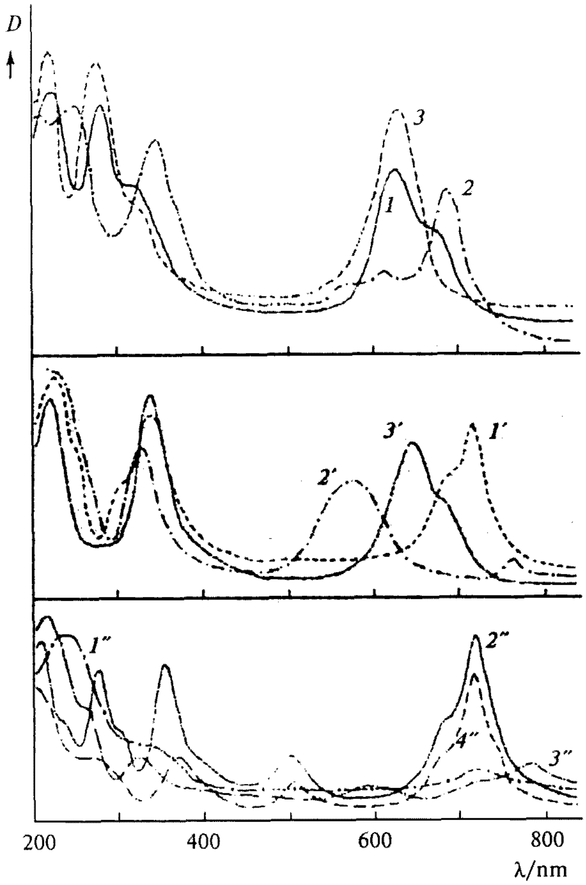

Fig. 2. Absorption spectra of cobalt 4,4′,4″,4‴-tetrabromophthalocyanine (*1—3*) and chloroaluminum phthalocyanine (*1′—3′*) films in the initial state (*1, 1′*), after treatment with nitrogen dioxide (*2, 2′*), and after subsequent treatment with ammonia (*3, 3′*). Spectrum of the chlorochromium phthalocyanine film after treatment with nitrogen dioxide (*1″*), spectrum of the initial chlorochromium 4,4′,4″,4‴-tetrabromophthalocyanine film (*2″*), and spectrum of this film treated with nitrogen dioxide (*3″*) and ammonia (*4″*).

thus stabilizing the radical cation. The experiments carried out in the reverse order do not provide similar result: the spectra of the films previously treated with ammonia and then with nitrogen dioxide are similar to those presented in Fig. 1 (curves *2* and *2′*), *i.e.*, they correspond to the $[MPc^*]^+$ form.

Phthalocyanines with altered coordination vacancies of the metal atom, namely, chloroaluminum phthalocyanine (AlClPc) and chlorochromium phthalocyanine (CrClPc), have also been studied.

Films of AlClPc acquire a crimson color on the treatment with NO_2 (see Fig. 2, curves *1′* and *2′*). The treatment with ammonia returns the film into its initial state. However, the spectrum of this film recorded after its subsequent annealing corresponds to curve *3′* in Fig. 2. This change in the spectrum may be caused either by an alteration of the crystal structure of the layer or, for example, by demetallation of the starting phthalocyanine. However, NO_2 is not removed initially from the film, and after the treatment with ammonia, the film most likely contains both reagents (in this case, presumably, reaction (1) does not proceed). This was also confirmed by the results of the measurements of the weight of molecules sorbed (microweighing) using the method of piezoelectric crystal resonator.[3]

The CrClPc films are immediately decolorized when exposed to nitrogen dioxide (see Fig. 2, curves *1″—4″*) and do not return to their initial state on treatment with ammonia or on annealing at 180 °C. Therefore, we have studied in detail films of chlorochromium 4,4′,4″,4‴-tetrabromophthalocyanine ($CrClPcBr_4$), which exhibits a similar spectrum (slight bathochromic shifts of the bands are observed, see curve *2″* in Fig. 2) and is more resistant to NO_2. From Fig. 2 it follows that in this case, too, the treatment with ammonia results in the regeneration of the phthalocyanine (the spectrum virtually coincides with the initial one, except for a shift of the Soret band to longer wavelengths and a general decrease in the absorption in the UV region); no formation of any intermediate complex is observed.

Thus, the treatment of sublimed MPc layers with nitrogen dioxide and ammonia obeys the main oxidation and coordination rules valid for solutions of phthalocyanines, and this implies that these films are highly gas permeable. Successive action of NO_2 and NH_3 ($p >$ 40 Torr) may result in the formation of octahedral phthalocyanine complexes in which the metal atom is capable of coordinating two extra NH_3 ligands, which are arranged symmetrically, perpendicular to the plane of the macrocyclic ligand. The stability of these complexes depends on structural factors.

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Preparation of *N*-nitrohydroxylamines by substitutive nitration

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Interaction of Na- or K-salts of *N*-acetyl-*N*-methylhydroxylamines with acyl or aryl halides results in corresponding *O*-substituted *N*-acetyl-*N*-methylhydroxylamines. Nitration of these compounds by nitronium salts or dinitrogen pentoxide results in *O*-substituted *N*-methyl-*N*-nitrohydroxylamines.

Key words: *N*-acetylhydroxylamines, substitutive nitration; *N*-nitrohydroxylamines; nitronium salts, dinitrogen pentoxide.

Earlier, it has been shown that *N*-nitrohydroxylamines (NHA) of the general formula $R^1N(NO_2)OR^2$ (where R^1 is alkyl, R^2 is benzoyl or nitroaryl) can be obtained by direct nitration of the corresponding *N,O*-disubstituted hydroxylamines (HA) by nitronium salts or by a mixture of nitric acid and acetic anhydride.[1,2] This procedure is of limited application since it is known that certain NHA are unstable under the action of acids.[1] Moreover, the preparation of *N,O*-disubstituted HA involves the introduction of protective groups. Here we describe the synthesis of NHA by substitutive nitration of *N*-acetyl-*N,O*-disubstituted HA, which occurs at a minimum acidity. The starting compounds, *i.e.*, *N*-acetyl-HA, are obtained without formation of intermediate *N,O*-disubstituted HA.

N-Acetyl-*N*-methyl-*O*-substituted HA **1a—d** have been used as the substrates of nitration. Compound **1a** can be easily obtained from *N*-methyl-HA hydrochloride and acetic anhydride.[3] Hydroxylamines **1b—d** were synthesized by the reaction of the corresponding halides with the potassium or sodium salt of *N*-acetyl-*N*-methyl-HA. (These salts are formed on treatment of compound **1a** with sodium alkoxides or KOH.) With different nitrating agents, the corresponding NHAs **2a—d** were obtained in all cases.

$$\underset{\mathbf{1a-d}}{\mathrm{MeN(COMe)OR}} \xrightarrow{NO_2^+} \underset{\mathbf{2a-d}}{\mathrm{MeN(NO_2)OR}}$$

R = Ac (**a**), MeOCO (**b**), $C_6H_4(NO_2)_2$ (**c**), $C_6H_3(NO_2)_3$ (**d**)

NO_2BF_4, a complex of NO_2BF_4 with 3,5-lutidine, $(NO_2)_2SiF_6$, and N_2O_5 were used to nitrate compounds **1a** and **1c**. The reaction with NO_2BF_4 in acetonitrile at −5 °C resulted in rather rapid disappearance of the starting HA from the mixture and the formation of new compounds (according to TLC). Following aqueous workup and extraction with chloroform, nitration products **2a** and **2c** were isolated. Compound **2c** proved to be identical with a product of independent synthesis.[2] As to compound **2a**, its spectral characteristics were in agreement with the expected structure, but it was rather unstable and decomposed completely at 20 °C in 1—2 h. Supposing that the decomposition of this compound is caused by traces of acid, we treated the reaction mixture with an aqueous solution of $NaHCO_3$; in this manner we succeeded in isolating quite a stable product. The acid that destroys NHA **2a** is BF_3, which seems to be generated upon decomposition of acetyl

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