Effect of peripheral substitution of copper phthalocyanine molecules on the electroconductivity in thin films during interaction with ammonia

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A decrease in the ability for oxygen bonding of PcCu molecules in peripheral substitution has been studied by measurements of conductivity in the presence of ammonia.

Key words: phthalocyanines, derivatives, conductivity, oxygen.

Many theoretical[1—3] (problems of electron transfer in doping from gaseous phases, catalysis, *etc.*) and practical studies, including those on designing resistive thin-film chemical sensors[4—6] based on metallophthalocyanines (PcM), are devoted to studying the interaction between PcM and gaseous sorbates (O_2, NH_3, NO_x, and others). In particular, it has been established that thin polycrystalline PcM films are p-type semiconductors, which is caused, as a rule, by the inevitable content of a acceptor admixture, oxygen,[1—4] whose effect can be excluded only by special procedures in ultra-high vacuum.[1,2] The addition of donating admixtures (vapor of Li, NH_3, H_2O, and others) decreases the conductivity (σ) of a layer up to the change (inversion) of the type of conductivity with an excess concentration of an electron donor due to the compensation of the oxygen effect.[1] There is also a chemical viewpoint with respect to similar phenomena: oxygen is coordinated to a metal atom of the phthalocyanine molecule to form the complex, which can serve as a trap for an electron.

$$\mathrm{PcM} + \mathrm{O_2} \rightarrow \mathrm{PcM{-}O_2}$$

$$\mathrm{PcM{-}O_2} + \bar{e} \rightarrow \mathrm{PcM{-}O_2^-}$$

These processes are described in detail.[2—4] In particular, it is shown that oxygen exists in the nondissociated form, and the PcM—O_2 bond strength depends on the ability of the metal to react with axial ligands. For similar PcM, the content of O_2 also depends on the crystal modification and to a substantial extent on the purity of the Pc-sample.[1,2] It is mentioned that the initial conductivity σ_0 of thoroughly degassed samples is very low, *i.e.*, the σ_0 value can be considered to be proportional to the concentration of the bound O_2 under certain conditions. The ESR method, which is widely used for studying "PcM—O_2" complexes (see Refs. 2 and 3), is technically complicated and gives hardly decoded signals in the case of real systems "thin sublimated film of a PcCu-derivative in the presence of NH_3". Therefore, the results of the measurements of the layer conductivity will be used in further discussions, especially as they have particular significance in practice.

Experimental

Copper(II) phthalocyanine, PcCu; copper(II) 4,4',4'',4'''-tetrabromophthalocyanine, Br_4PcCu; copper(II) 4,4',4'',4'''-tetrachlorophthalocyanine, Cl_4PcCu; and polychlorinated copper phthalocyanine, whose molecule contains 14—16 chlorine atoms, Cl*PcCu (see Ref. 5) were used. PcCu and Cl*PcCu are industrial pigments ("phthalocyanine blue" and "green", respectively) that were preliminarily purified by recrystallization from conc. H_2SO_4; Br_4PcCu and Cl_4PcCu were synthesized at the Ivanovo Institute of Chemical Technology by the Wilder method.[7] All phthalocyanines studied were additionally purified by vacuum sublimation. Thin polycrystalline films were obtained by thermal evaporation in a high vacuum (on a VUP-5 installation) onto substrates at ~20 °C (α-form).[1—3] The substrates were optical quartz glasses for measuring electron absorption spectra (EAS) or dielectric plates of devitrified glass (such as Pyroceram) with raster Nichrome contacts for measuring conductivity.[1,5,6] The mass of the sorbing gas was additionally measured by the method of piezoquartz resonant microweighing.[5,6] All dark measurements were carried out in a specially designed cell in a static regime at ~20 °C and an initial vacuum of 10^{-6} to 10^{-7} Torr.[6] Films were ~150 nm thick, and all of them were evacuated at 160 to 180 °C for 2 h prior to measurements.

Results and Discussion

It was established that the EAS of the films studied undergo no substantial changes in the presence of NH_3, which indicates the absence of strong interaction involving the π-system of the phthalocyanine macrocycle. No charge-transfer bands typical of reflectance spectra[1—3] are observed in the 800 to 1200 nm long-wave spectral range (which is confirmed by the results of IR

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spectroscopy). Only a very weak increase in absorption at 900 to 920 nm is found, which is likely due to some forbidden transitions perpendicular to the plane of the π-electron phthalocyanine macrocycle. However, a noticeable bathochromic shift of the Q-band[2] (which is less pronounced with the Soret band) is observed in the initial spectra ($p_{NH_3} = 0$) on going from PcCu to Cl*PcCu (see Refs. 2 and 7): $\Delta\lambda$ is 7 and 4 nm for Br_4PcCu and Cl_4PcCu, respectively, and 33 nm for Cl*PcCu. The long-wave shift is accompanied by a decrease in the total optical density of layers of equal thickness (hypochromic effect). This means that, first, the extent of the π-electron delocalization over the whole Pc-macroligand, including the benzene rings, is rather high[2,3] and, second, the energy of the corresponding π—π*-transition decreases under the effect of auxochromic substituents, which results in depletion of the π-electron density of the C—N-macroring.[7] Thus, it can be assumed that the inductive effect known in organic chemistry is observed: strongly electronegative halogen atoms withdraw a portion of the electron density to decrease δ^- near the metal atom. It is evident that similar changes exert an effect on the "PcM—O_2" bond strength, and since oxygen is an electron acceptor itself, the assumed enhancement of acceptor properties of the Pc-macroligand should result in weakening of this bond.

This assumption finds an interesting experimental confirmation. The dependences of logσ of the Pc-layer on the ammonia pressure p_{NH_3} for the derivatives studied are presented in Fig. 1. It should be immediately emphasized that the additionally obtained dependences of the number (mass) of sorbed gas molecules on the thickness of the layer and the kinetic curves for each static point in Fig. 1 suggest that the whole volume of the film participates in the process and all processes described are volume processes.

In the case of initial PcCu (see Fig. 1, curve *1*) a drastic decrease[4] in σ is observed at low p_{NH_3}, which is explained by the compensation of the O_2 effect (see above). At increased pressures the decrease in σ is retarded, and the recompensation (the inversion of the sign of carriers) of the "oxygen effect" occurs when the film is saturated with a donating agent (NH_3). In the case of Cl*PcCu (see Fig. 1, curve *2*), σ increases when the gas is introduced similar to the described[6] process of the interaction between Cl*PcCu films and AsH_3. Taking into account this specific feature and a lower initial conductivity σ_0 at $p_{NH_3} = 0$ ($\sim 3 \cdot 10^{-9}$ Ohm^{-1} cm^{-1} compared to $6 \cdot 10^{-6}$ Ohm^{-1} cm^{-1} for PcCu, see Fig. 1), one can believe in accordance with the previous study[6] that the initial thin-film sample of Cl*PcCu is the n-type semiconductor under these conditions and, hence, it does not contain bound oxygen.

For Br_4PcCu, which is the intermediate in degree of substitution member of the series, σ decreases first like that in the case of PcCu, but at $p_{NH_3} > 15$ Torr σ increases noticeably as p_{NH_3} increases (see Fig. 1, curve *3*), which is typical of Cl*PcCu. Since the experimental technique is strictly unified, this result can be explained only by the fact that Br_4PcCu films contain bound O_2, but its amount is considerably lower than that in initial PcCu. This means that, first, as has been assumed, the peripheral substitution decreases the ability of the PcCu molecule to adsorb oxygen and, second, the energy of the "$Br_4PcCu—O_2$" bond is comparable to kT. It should be noted that according to the literature data,[1] the energy of the "PcCu—O_2" bond for the surface of the β-monocrystalline sample is estimated as equal to 1 eV.

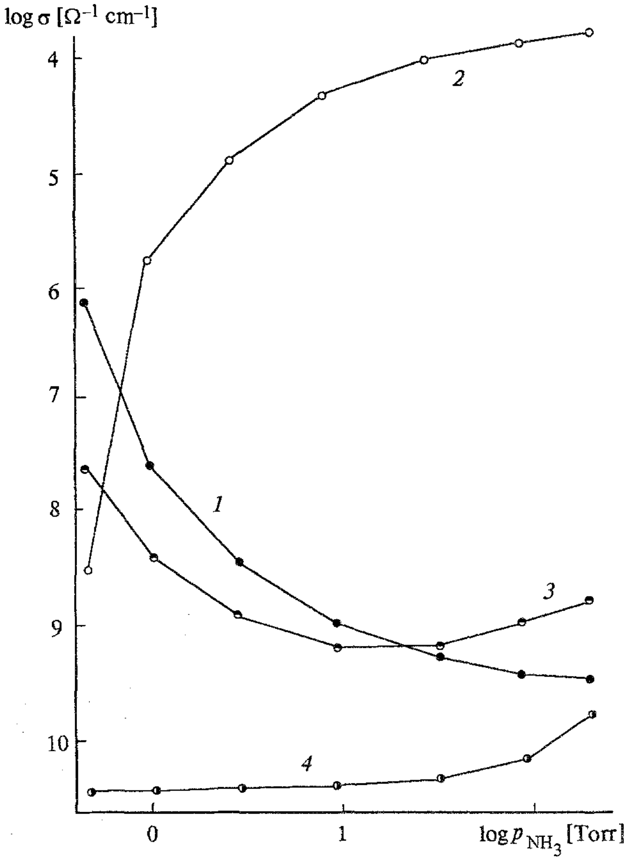

Fig. 1. Dependence of conductivity σ on the ammonia pressure p_{NH_3} for films of PcCu (*1*), Cl*PcCu (*2*), Br_4PcCu (*3*), and Cl_4PcCu (*4*).

For Cl_4PcCu (see Fig. 1, curve *4*), the shape of the dependence is nearly the same as that of Br_4PcCu; however, absolute values of σ are very low. This coincides with the assumption that films of tetrasubstituted PcCu contain a small amount of O_2. In this sense, σ_0 of Br_4PcCu films is anomalously high, which can be related to the change in packing (for example, a decrease in intermolecular distances) in the Pc-layer for substitution by bulky Br atoms: the van der Waals radius of the Cl atom is equal to 0.178 nm, which is 0.015 nm lower than the corresponding value[8] of the Br atom, and the distance between the planes of molecules in nonsubstituted PcCu is only 0.34 nm.[2]

Thus, it follows from the data presented that the substitution of only one atom in each isoindole fragment of the phthalocyanine macroligand results in a noticeable change in the physical (spectral and conducting) properties of PcCu films. In the given case, we can deliberately change the phase (macro-) properties of Pc-films, in particular, the response of conductivity to the gas action, modifying the initial PcM-complex at the molecular level. Even insignificant change in chemical structure directly affects the electrophysical parameters of an object. Taking into account the fact that thin-film structures based on phthalocyanines are presently promising materials for resistive-type chemical sensors, the peripheral substitution of the Pc-macromolecule can be considered to be one of the ways for creating optimally sensitive layers of chemical sensors for gas analysis.

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References

1. H. Laurs and G. Heiland, *Thin Solid Films,* 1987, **149**, 129.
2. J. Simon and J.-J. Andre, *Molecular Semiconductors,* Springer, Berlin, 1985.
3. M. R. Tarasevich and K. A. Radyushkina, *Kataliz i elektrokataliz porfirinami* [*Catalysis and Electrocatalysis by Porphyrins*], Nauka, Moscow, 1982 (in Russian).
4. A. Wilson and R. A. Collins, *Phys. Stat. Sol. (a)*, 1986, **98**, 633.
5. L. G. Pakhomov, A. V. Belyaev, and G. L. Pakhomov, *Abstr. of the 1st Conf. on Gas Sensors*, Vilnius, October 5—8, 1993, 34.
6. Ya. A. Fel', Ph. D. (Phys.-Mat. Sci.) Thesis, Institute of Chemistry at Nizhnii Novgorod University, Nizhnii Novgorod, 1991 (in Russian).
7. G. P. Shaposhnikov, V. F. Borodkin, and M. I. Fedorov, *Izv. Vuz., Khim. Khim. Tekhnol.* [*Bull. Institutions of Higher Learning, Chemistry and Chem. Technology*], 1981, **24**, 1485 (in Russian).
8. A. I. Kitaigorodskii, *Kristallokhimiya* [*Crystal Chemistry*], Mir, Moscow, 1971 (in Russian).

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