Experimental

IR, NMR, and mass spectra were recorded on Bruker IFS-113, Bruker CXP-200, and Finnigan GS/MS-4021 instruments, respectively.

Epichlorohydrin (2.36 g, 0.0257 mol) and triethylamine (0.43 g, 0.0043 mol) were placed in a jacketed three-neck flask flushed with carbon dioxide. The flask was equipped with a reflux condenser with a rubber balloon filled with an excess of CO_2. The reaction mixture was heated at 60 °C in the atmosphere of CO_2 and stirred for 5 h. After distillation of the reaction mixture, chloromethylethylene carbonate (3.39 g, 99.4%) with b.p. 145—148 °C (10 Torr) was obtained. IR (CH_2Cl_2), ν/cm^{-1}: 1817—1818 (C=O). ^{1}H NMR (200 MHz, $CDCl_3$, Me_4Si), δ: 3.75 (m, 2 H, OCH_2); 4.36 (m, 1 H, CHCl); 4.56 (m, 1 H, CHCl); 5.00 (m, 1 H, OCH). ^{13}C NMR (50.3 MHz, $CDCl_3$, Me_4Si), δ: 44.1 (t, CH_2Cl); 66.8 (t, OCH_2); 74.4 (d, OCH); 154.4 (s, C=O). MS (EI, 70 eV), *m/z* : 136, 138 $[M]^+$.

Reactions with other bases used as catalysts were performed according to the same procedure. The yields of the product were determined without its isolation, by IR spectroscopy using a calibration line.

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Action of gaseous ammonia and water on neodymium diphthalocyanine

P. N. Moskalev and A. I. Sibilev*

B. P. Konstantinov St. Petersburg Institute of Nuclear Physics, Russian Academy of Sciences,
188350 Gatchina, Leningrad Region, Russian Federation.
Fax: +7 (812) 713 6025. E-mail: moskalev@hep486.pnpi.spb.ru

The method of flow injection into the gas flow with detection of current resistance of the film was used to investigate the action of ammonia and water vapor on neodymium diphthalocyanine film. The value and sign of the electrophysical response are reversible at 18—22 °C. When the film contacts with vapor, the current is changed within a few seconds, whereas the relaxation to the initial value when vapor is removed occurs within tens of seconds. The response parameters are suitable for developing effective sensors based on resistant films. No optical changes in the absorption spectra of the films were observed in the 400—800 nm region under the action of ammonia and water vapor.

Key words: phthalocyanine, neodymium; conductivity; ammonia, water, gas.

Metallophthalocyanines[1] can be used as gas-sensitive films toward ammonia vapor.[2,3] We have recently obtained metallodiphthalocyanines of rare-earth elements (REE), actinides, hafnium, and zirconium.[4] Films of these sandwich-type compounds were shown to be sensitive to the action of both strong electron donors (metallic sodium vapor[5]) and acceptors (NO_2 and I_2 vapor[6,7]). In this work, we studied the gas sensitivity of neodymium diphthalocyanine films PcNdPc$^{\cdot}$ (where Pc$^{\cdot}$ = $(C_{32}H_{16}N_8)^{1-}$, Pc = $(C_{32}H_{16}N_8)^{2-}$) to the action of vapor of relatively weak electron donors and acceptors such as ammonia and water. Compared to other metallophthalocyanines, these compounds show lower activation energies of conductivity, different patterns of

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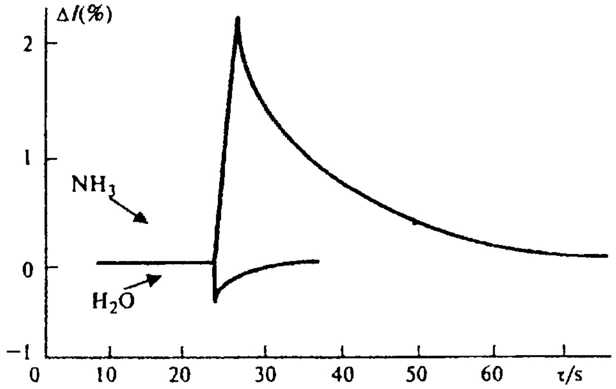

Fig. 1. Dynamics of the change in the electric current through the PcNdPc˙ film (ΔI (%)) during pulse injection of ammonia or water vapor into the dry air flowing around the film.

conductivity,[8] a unique OD structure,[9] and an open crystalline lattice favoring easy penetration of vapor into the bulk film.

Experimental

Electrophysical studies were performed by pulse flow injection (FI) of ammonia (0.3—0.03 mg per pulse) or water (0.2—0.02 mg per pulse) into the dry air flowing around the metallodiphthalocyanine film. The air flow dried with KOH was passed with a velocity of 15—20 L h^{-1} into a 3-cm^3 chamber for vapor injection and into the next chamber with the same volume containing a sensitive element, which consisted of a ceramic base covered with Nichrome film with ohmic gap. The ohmic gap was filled by rubbing with a film (~10 μm thick) of the substance under study. The ohmic resistance of the PcNdPc˙ film was 10^5 Ohm at 18—22 °C. The voltage dependence of the current through the film obeys Ohm's law within the 1—10 V range. A flow-type gas cell was used in the spectral studies. The film of the substance under study was rubbed on the inner surface of the cell window, which made it possible to detect the absorption spectra of the film during the process and after the action of ammonia or water vapor. The highest concentration of ammonia or water in the air flow through the cell reached values of 0.3 and 0.2 mg cm^{-3}, respectively. The duration of contact between the film and vapor was not shorter than 30 min.

Results and Discussion

The analysis of the dynamics of the ammonia and water vapor action in the FI method (Fig. 1) indicates that the current value through the film is reversibly changed in the "air—vapor—air" cycles. In the stage of sorption by the film, ammonia increases and water vapor decreases the current value. The explanation is that ammonia acts with respect to PcNdPc˙ as the electron donor, which increases the number of current carriers in the film, while water vapor is the electron acceptor and thus decreases the number of current carriers in the film.

Preliminary experiments established that the dynamics describing desorption of ammonia and water in the given flow of dry air is independent of its rate and, hence, determined by the nature of the film and the stability of the compound with ammonia and water that was formed in the bulk film. Using the graphic Wilkinson method,[10] we calculated the rate order and rate constant of the processes observed shown in Fig. 1 as descending branches of the FI curves. The kinetic curve of water desorption obeys a first-order equation with the rate constant of $5 \cdot 10^{-1}$ s^{-1}. A similar process of ammonia desorption is satisfactorily described by the kinetic equation with a higher order close to two with a rate constant equal to $2 \cdot 10^{-1}$ $\mu A^{-1} s^{-1}$.

The experiments in the gas cell showed that the absorption spectrum of the film in the region of 400—800 nm remains unchanged in the presence of vapor of dry ammonia and water. Vapor of metallic sodium reduces metallodiphthalocyanine in the film to the anion,[5] and vapor of I_2[6] and NO_2[7] forms cation-type complexes. This results in a substantial change in the absorption spectra in the 400—800 nm region of the metallodiphthalocyanine film. The change is due to the participation of the π-system of phthalocyanine in the electron transfer in donor—acceptor interactions. Since, as it has been established, neither ammonia nor water vapor change the spectral parameters of the PcNdPc˙ film in the region of electron transitions of 400—800 nm, one may assume that electrons and energy levels from the conductivity band of the film participate in the donor—acceptor interaction. Therefore, along with the change in the electrophysical properties, one should expect spectral changes in the region of the intermolecular charge transfer band of the metal diphthalocyanine films (3800 cm^{-1}).[11]

Thus, the results of the present work and published data presented allow us to recommend sandwich-type metallodiphthalocyanines as materials for sensors for gaseous media containing substances to be determined as donor—acceptor type molecules.

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Synthesis of lithium octahydrotriborate solvates with dioxane

L. V. Titov, L. A. Gavrilova, and L. V. Zhemchugova*

Institute of New Chemical Problems, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 742 0004

A method for the synthesis of lithium octahydrotriborate in the form of solvates with dioxane containing one, two, and four dioxane molecules was developed.

Key words: octahydrotriborate, pentaborane(9), diborane, tetrahydrofuran, dioxane, solvate.

Salts of octahydrotriborates with alkali metal cations (Na, K, Rb, and Cs) are known in the nonsolvated state[1–3] and in the form of solvates with dioxane (Dx): $NaB_3H_8 \cdot 3\ Dx$, $NaB_3H_8 \cdot Dx$,[3–4] and $KB_3H_8 \cdot 2.5\ Dx$.[5] The following solvated alkali-earth octahydrotriborates were synthesized: $Mg(B_3H_8)_2 \cdot 6\ NH_3$,[6] $Mg(B_3H_8)_2 \cdot 2\ DG$, $Ca(BH_4)(B_3H_8) \cdot 2\ DG$, and $Sr(B_3H_8)_2 \cdot 3\ DG$,[7] where DG is diethylene glycol dimethyl ether (diglyme), and tetraalkylammonium octahydrotriborates $R_4NB_3H_8$ (R = Me, Et, and Bu).[8]

LiB_3H_8 (**1**) is known to exist only as an ethereal solution. Compound **1** was previously synthesized[1] by the exchange reaction of nonsolvated NaB_3H_8 with LiBr in ether and THF; however, it was not isolated in the solid state.

This work is devoted to the synthesis of lithium octahydrotriborate in the form of solid solvates $LiB_3H_8 \cdot n$Dx and to the study of conditions of their desolvation.

Experimental

$NaB_3H_8 \cdot 3Dx$ (**2**) and LiBr were the starting compounds for the synthesis of $LiB_3H_8 \cdot n$Dx. The reaction was performed in THF at 20 °C. Prior to use, the starting compound **2** was recrystallized from 2-propanol. The resulting material contained 98.5% of the main compound; the purity of LiBr was 99.0%. Before the synthesis, THF was dried by refluxing over KOH and distilled from $LiAlH_4$.

Synthesis of solvates of lithium octahydrotriborate with dioxane $LiB_3H_8 \cdot n$Dx. A solution of LiBr (1.93 g, 22.2 mmol) in THF (10 mL) was added dropwise to a solution of compound **2** (7.32 g, 22.3 mmol) in THF (60 mL). A precipitate of NaBr was immediately formed. The mixture was stirred for 2—3 h, the precipitate was filtered off, and the filtrate was concentrated approximately to half its original volume. Dioxane was added to the solution obtained, and the precipitation of crystals of tetrasolvate $LiB_3H_8 \cdot 4\ Dx$ (**1a**) (yield 7.4 g, 86%) occurred during concentration of its solution. Found (%): Li, 1.85; B, 8.11; H_{hydr}, 2.28. $LiB_3H_{8(hydr)} \cdot C_{16}H_{32}O_8$. Calculated (%): Li, 1.80; B, 8.45; H_{hydr}, 2.10. IR ν/cm^{-1}: 2470 s, 2440 s, 2400 s, 2370 sh, 2120, 2070, 1450, 1300, 1260, 1160, 1120, 1080, 1050, 1020, 890, 870, 640.

At 20 °C in vacuum, tetradioxanate is easily transformed into bisdioxanate $LiB_3H_8 \cdot 2Dx$ (**1b**).

When the mixed solvent (THF and dioxane) was completely distilled off, **1b** with admixture of LiBr and **2** was isolated in the solid phase. To purify **1b**, a small amount of benzene was added to the concentrated solution, and the precipitate of **2** was separated by filtration. The solution obtained was concentrated to dryness, and compound **1b** was extracted with ether from the residue. After separation of ether-insoluble LiBr and removal of the ether, **1b** was obtained. Found (%): Li, 3.15; B, 13.51; H_{hydr}, 3.84. $LiB_3H_{8(hydr)} \cdot C_8H_{16}O_4$. Calculated (%): Li, 3.22; B, 15.04; H_{hydr}, 3.74. IR, ν/cm^{-1}: 2480 s, 2440 s, 2420 s, 2360 sh, 2160 w, 2100, 1450, 1300, 1260, 1160, 1120, 1080, 1050, 1020, 890, 870, 640.

Compound **1b** is a white crystalline product, which is stable in vacuum up to 65 °C, well soluble in water without decomposition, soluble in THF, ether, and 2-propanol, and poorly soluble in benzene.

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