IR SPECTRA, ELECTRONIC CONFIGURATION, AND PHYSICOCHEMICAL
CONVERSIONS OF TRIANIONS OF NICKEL OCTAETHYLPORPHIN
IN THE SOLID PHASE

N. V. Ivashin

On the basis of an investigation of IR spectra, it has been found that trianions of Ni octaethylporphin, when there is a change in their phase state in the series from solution to film, are capable of entering into a reaction of partial anion-cation recombination, resulting in the formation of dianions with two additional electrons located on the porphyrin macroring, rather than one electron, as is the case when the dianions are obtained directly. Conditions have been found for stabilization of the trianions of Ni-octaethylporphin in the solid phase and their electronic configuration has been established; this includes the positioning of two additional electrons in \( \pi \)-orbitals of the macroring and one additional electron in the \( d_{x^2-y^2} \) orbital of the central metal atom.

Study of the conditions of stabilization, the electronic configuration, and the physicochemical and spectroscopic properties of anion-radical and anion forms of porphyrins in various states of aggregation is a necessary stage in elucidating the role of ionic forms in reactions involving porphyrins and in the control of these reactions. Such studies are also important from the standpoint of modifying the electronic structure of these compounds, which are finding more and more applications in science and technology [1]. The information that has been accumulated up to the present time on the spectroscopic manifestations (electronic, ESR, NMR, IR, and resonance Raman scattering spectra) pertains mainly to a type of reduction of porphyrins such that the additional electronic charge is distributed through the \( \pi \)-conjugated system of bonds of the porphyrin macroring [2, 3]. Very little information has been reported from any spectroscopic studies of the anionic forms of porphyrin complexes with transition metals — in which additional electrons may occupy d-orbitals of the central metal atom — in comparison with the \( \pi \)-anions [4, 11].

For the Ni-octaethylporphin (Ni-OEP), electronic spectra of the anionic forms were investigated in [10], and IR spectra in [12]. From the electronic absorption spectra it was established that the electronic configuration of the monoanion (in solution) is characterized by the presence of an additional electron in the d-orbital of the central metal atom; for the dianions and trianions, one electron occupies the d-orbital of the metal, and the remainder of the additional charge is localized on the porphyrin macroring. From

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the results obtained in a previous study [12] of the IR absorption spectra of the monoanionic and dianionic forms of Ni-OEP (and also the monoanionic form of Co-OEP), it was concluded that the method is sensitive not only to occupation of a vacant \( \pi \)-orbital by additional electrons, but also to occupation of \( d \)-orbitals of metalloporphyrins; also, it was demonstrated that the spectral changes taking place upon transition to anions with different electronic configurations are not identical in character. Also found were spectral manifestations of the interaction of anions with \( Na^+ \) countercations and the capability of Ni-OEP monoanions for existence in \( d \)- and \( \pi \)-electronic configurations, depending on their phase state (solution or film) and depending on the crystal modification in the solid phase.

In the present work, we studied the conditions for stabilization of Na-OEP trianions in the solid phase and their electronic configuration; the data reported here provide evidence that Ni-OEP trianions are capable of entering into a reaction of partial recombination with alkali metal countercations when there is a change in the phase state of the material. As in [10, 12], the anions were generated by the interaction of degassed solutions of Ni-OEP in tetrahydrofuran with an alkali metal mirror. The IR spectra were measured on films prepared by freezing out the solvent from the reaction cuvette.

In the process of drying the film obtained from a solution of trianions 3 \( Na^+ \), Ni\(^{2-} \) (OEP), the film color changes from green to red. This may be related to physicochemical conversions of the trianions that are accompanied (for example) by a change in their electronic configuration [12]. With the aim of clarifying this question, we undertook an investigation, by analogy with [12], of the influence of alkali metal countercation type and the effect of heating the specimens on the IR spectra of the trianions. In this case, when a film obtained from a solution of the trianions is not preheated and is then washed off, the electronic absorption spectrum of the solution essentially coincides with that of the trianions. Heating of the film does not lead to any appreciable changes in the IR spectrum (Fig. 1, spectra b and b'). Along with this, the electronic absorption spectrum of a solution obtained after washing off such a specimen (Fig. 2, spectrum b) differs from the original spectrum, no longer corresponding to the trianionic form but rather the dianionic form. The assignment of this product to the dianionic form is supported by a comparison of its IR spectrum with that of dianions generated in the process of successive contact.