INFRARED SPECTRA AND ELECTRONIC CONFIGURATION
OF ANIONIC FORMS OF NICKEL AND COBALT OCTAETHYLPORPHIN
IN THE SOLID PHASE

N. V. Ivashin and I. V. Filatov

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On the basis of an investigation of IR spectra, electronic configurations have been established for the monoanions of Ni and Co octaethylporphin and the dianion of Ni octaethylporphin in the solid phase; characteristic features have been revealed in the effects on the IR spectra of metalloporphyrins from occupancy of their vacant $d_z^2$ and $d_{x^2-y^2}$ orbitals by additional electrons. It has been shown that interaction of the anions with alkali metal countercations may lead (depending on the electronic configuration of the anion and the type of cation) to activation of bands of composite vibrations in the IR spectrum. It has been found that the monoanions of Ni octaethylporphin are capable of existing in $d$- and $\pi$-electronic configurations, depending on the phase state (solution or film) and the crystal modification in the solid phase.

Spectroscopic studies of the ionization of porphyrins to the anionic or cationic forms are necessary on the one hand for the development of methods of product identification in redox reactions and, on the other hand, for definition of the electronic structure of these forms and the dependence of electronic structure on various internal and external factors. Solution of these problems should ultimately provide favorable conditions for elucidating the role of the ionic forms in processes involving porphyrins, and for control of these processes [1].

In a study of the electronic spectra of products from the reduction of Ni and Co octaethylporphin (Ni-OEP, Co-OEP) in tetrahydrofuran on a sodium mirror [2], it was shown that (in contrast to Zn complexes of porphyrins) the first additional electron occupies an orbital localized primarily on the central metal atom. The present work has been aimed at investigating the electronic configuration of monoanions of Ni-OEP and Co-OEP and the dianion of Ni-OEP in the solid phase; the work has been further aimed at revealing the characteristic features of the effects on the IR spectra of metalloporphyrins from occupation of the $d$-orbitals of the central metal atom by additional electrons, in contrast to the previously investigated cases of $\pi$-occupancy [3-5]. We have also examined the question of how the IR spectra of the anions in different electronic configurations are influenced...
by the type of alkali metal countercation (Na\(^+\), K\(^+\)) and by temperature-related phase transitions.

The anionic forms of Ni-OEP and Co-OEP were obtained by interaction of their degassed solutions in tetrahydrofuran with an alkali metal mirror. The course of the reaction was monitored on the basis of electronic absorption spectra [2]. The IR spectra were measured on films prepared in the process of freezing out the solvent from the reaction cuvette [5]. Solvent retention in the samples was judged on the basis of IR spectral manifestation of the most intense absorption bands of tetrahydrofuran in the region of the spectrum that was investigated - bands at about 920 and 1080 cm\(^{-1}\). Analysis of the IR spectra indicates that the solvent molecules are weakly bound in the anions in the film and that they can be completely removed from the sample.

**Ni Octaethylporphin.** According to the results obtained in an investigation of resonance Raman scattering spectra [6] and data obtained by x-ray structure analysis [7, 8], Ni-OEP can exist in the solid phase in two different crystal modifications, one of which has been assigned to a triclinic form with D\(_{4h}\) symmetry, the other to a tetragonal form with D\(_{2d}\) symmetry. The geometric parameters of these forms of Ni-OEP differ considerably; for the Ni-OEP (D\(_{4h}\)), the bonds of the porphyrin framework are longer and the force constants correspondingly smaller in comparison with the Ni-OEP (D\(_{2d}\)). Such structural rearrangements related to a change in the polycrystalline structure of the specimen could be manifested in the IR spectra of the anions, together with effects due to the addition of electrons. With the aim of determining the possibility of spectral detection, we measured the IR spectra of the products of regeneration of the anionic forms and the IR spectra of the polymorphic modifications of Ni-OEP.

The main product from regeneration of the porphyrin anions in air consists of neutral molecules of the original compound. Along with this, it appears, the polycrystalline structure of the films is not broken down in the process of regeneration of the anions, and the IR spectra of the regeneration products preserve information on the polycrystalline structure of the anions. In accordance with this hypothesis, we registered not one but two spectral forms for the products obtained by the regeneration of the Ni-OEP anions. The same spectral forms were found when the method of preparing the solid samples of neutral Ni-OEP was varied (Fig. 1). One of these forms is assigned to Ni-OEP purified by recrystallization in chloroform and pressed in a KBr matrix; the other form pertains to Ni-OEP sublimed on a KBr substrate at room temperature. A comparison with literature data on the resonance Raman scattering spectra and the results obtained by x-ray structure analysis provides grounds for assigning the first form to a tetragonal crystal modification, the second form to a triclinic modification. As can be seen from Fig. 1, the spectra of the two forms are very definitely different and the spectra can be used to determine the type of polycrystalline structure of solid samples of the anionic forms of Ni-OEP.

The results of this analysis indicate that the monoanionic and dianionic forms of Ni-OEP with Na\(^+\) countercations (Na\(^+\) and Ni-OEP\(^-\), 2 Na\(^+\) and Ni-OEP\(^{2-}\)) in a film form the triclinic crystal modification and, hence, have the same molecular symmetry D\(_{4h}\) as that of the previously investigated π-anions of Zn-OEP [4, 5]. Occupancy of a π-orbital of the porphyrin ligand by an additional electron is characterized by a considerable decrease in the vibration frequency γCH (837 → 790 cm\(^{-1}\)). When the change is made to the monoanionic form (Na\(^+\), Ni-OEP\(^-\)), the γCH vibration band of Ni-OEP at 830 cm\(^{-1}\) (Fig. 1, spectrum c') undergoes only a slight high-frequency shift (830 → 840 cm\(^{-1}\)). Such a substantial difference between Ni-OEP and Zn-OEP in the behavior of the γCH vibration frequencies upon ionization means that they differ in electronic configuration of their monoanions; hence, we can conclude that, in the case of Ni-OEP, the additional electron occupies the dx\(^2\)-y\(^2\) orbital of the central metal atom.

A considerable low-frequency shift in the γCH vibration band of Ni-OEP (830 → 780 cm\(^{-1}\)) is observed upon conversion to its dianionic form\(^a\) (Fig. 2a). This is on the same order of magnitude as for the monoanionic form of Zn-OEP. In the spectrum of the Ni-OEP dianion, we also find bands at approximately 1520 and 860 cm\(^{-1}\), characteristic for the monoanionic

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\(^a\)The same as in the case of the monoanionic form, the assignment we have made for the γCH vibration bands of the dianionic form is confirmed by an examination of the IR spectra of the neutral molecules and the anionic forms of the deuterium-substituted modification of Ni-OEP.