

Short communication

Spectroscopic studies of zinc(II)tetraphenylporphyrin molecular complex with 1,4-dioxane

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Abstract

The molecular complex of zinc(II)tetraphenylporphyrin with 1,4-dioxane has been obtained. The IR spectra of the $[\text{Zn}(\text{TPhP})(1,4\text{-dioxane})_2]$ stable molecular complex between 4000 and 50 cm^{-1} have been studied. An interpretation is given on the base the “chair” conformation of 1,4-dioxane molecule.

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1. Introduction

Studies of molecular complexes with electron donating ligands, such as 1,4-dioxane, are of a great scientific and practical interest. In 1990, 1,4-dioxane was recognized by US Environmental Protection Agency to be toxic for human life [1]. On the other hand, 1,4-dioxane is widely used in many industrial processes, perfumery, hardware (appliance) chemistry. Numerous biochemical data that were reported for the last 12 years revealed that even very small amounts of this solvent stimulate growth of malignant cells in living organisms. Due to rapid growth of coordination chemistry of metalloporphyrins, the proposed therapeutic uses of these compounds include the photodynamic therapy of cancer [2], inactivation of viruses [3], blood substitutes [4]. Synthetic metalloporphyrins can be applied as sorbents and antitoxic agents for hemosorption.

The interactions between zinc(II)tetraphenylporphyrin (ZnTPhP) and linear and cyclic ethers, aldehydes, ketones, lactones and alcohols in solutions have been studied in our previous works [5–7]. It has been found [7] that donor–acceptor complex of

ZnTPhP with 1,4-dioxane is the most thermodynamically stable. The structure of this new complex is not determined. Now the IR spectroscopy was proposed to study the bonding in it.

The IR spectra of the complex are presented in Figs. 1–3. The complexation between ZnTPhP and 1,4-dioxane is confirmed by the presence of bands assigned to 1,4-dioxane in the spectra of the samples (nujol mulls and crystalline films) studied. Small frequency shifts have been found in comparison of the spectra of the complex with those for individual components. The weak disturbances of the most frequencies and intensities are commensurable with the effects of crystal field.

The IR and Raman scattering spectra of liquid 1,4-dioxane have been studied and assigned earlier [8,9]. The vibrational spectra for ZnTPhP are also known [10]. Also IR and Raman spectra of NiTPhP were recorded and the normal coordinate treatment for isotope $^{14}\text{N}\text{--}^{15}\text{N}$, $^{12}\text{C}\text{--}^{13}\text{C}$, H–D $^{14}\text{N}\text{--}^{15}\text{N}$, $^{12}\text{C}\text{--}^{13}\text{C}$, H–D substituted molecule was performed in [11]. These works were taken into account in our spectroscopic study of the complex of ZnTPhP with 1,4-dioxane.

It should be noted that the ZnTPhP spectrum of the mulls are similar to that of ZnTPhP pellets in KBr published in [10]. Some small differences between the mulls as well between the mulls and the crystal films of ZnTPhP spectra may be attributed to polymorphism. Also in the mulls spectra the Christiansen effect is observed. However, no obvious indications of polymorphism

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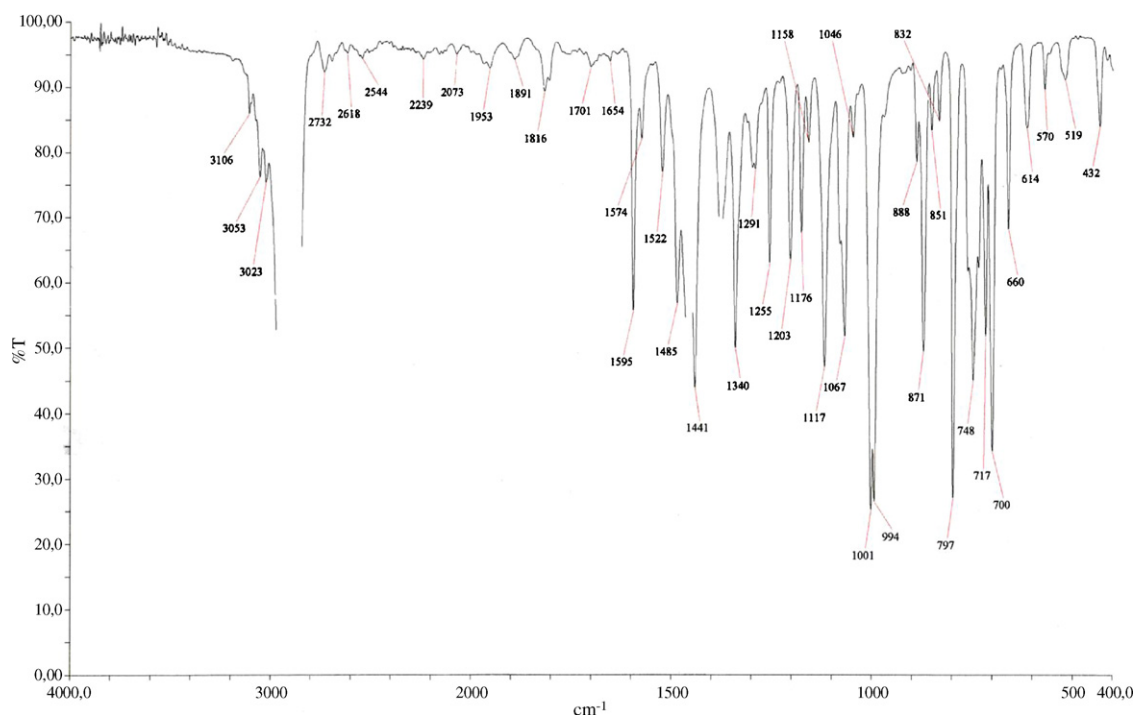


Fig. 1. FT IR spectrum of nujol mulls of $[\text{Zn}(\text{TPhP})(1,4\text{-dioxane})_2]$ crystalline complex in the $400\text{--}4000\text{ cm}^{-1}$ range. Baseline correction was used.

were found at the investigation of different samples (mulls and the crystal films on KBr and CsJ windows) of the $[\text{Zn}(\text{TPhP})(1,4\text{-dioxane})_2]$ complex (Figs. 1 and 2).

The frequencies of 1,4-dioxane for the $[\text{Zn}(\text{TPhP})(1,4\text{-dioxane})_2]$ complex are presented in Table 1. Their number is determined by symmetry of the molecule. The “chair”–“bath” conformational transformation should be accompanied by change of symmetry from C_{2h} to C_{2v} . (Fig. 4). The IR and Raman active number fundamentals for both the types of group symmetry are the next:

for C_{2h} : $\Gamma = 10 a_g (\text{R}) + 9 b_u (\text{IR}) + 9 a_u (\text{IR}) + 8 b_g (\text{R})$

for C_{2v} : $\Gamma = 10 a_1 (\text{IR, R}) + 9 a_2 (\text{R}) + 9 b_1 (\text{IR, R}) + 8 b_2 (\text{IR, R})$.

According to selection rule for of oriented gas model, the molecule of 1,4-dioxane must have 18 IR active fundamentals for the C_{2h} symmetry and 27 for the C_{2v} symmetry. Only 18 frequencies were found (Table 1). Hence, it likely that 1,4-dioxane molecule has the C_{2h} symmetry and the “chair” conformation in the crystal complex with ZnTPhP as in liquid 1,4-dioxane.

X-ray analysis of the complex [12] was performed after the spectral studies. These data will be published later. According to these unpublished data, the structural data confirm the “chair” conformation of both 1,4-dioxane molecules in the complex with ZnTPhP. These ligands are bound to Zn^{2+} ion each through one-oxygen atom. Unexpected result is their crystallographic nonequivalency and very different Zn–O distances (2.43 and 2.50 Å).

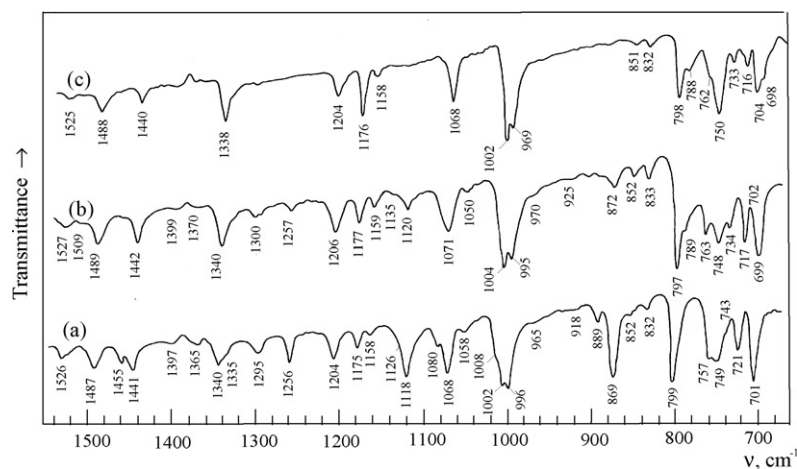


Fig. 2. Dependence of infrared spectra of crystalline films of ZnTPhP on KBr disk on 1,4-dioxane content. Mol.% 1,4-dioxane is 67 (a), 30 (b) and 0 (c).

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