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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 [Zn(TPhP)(1,4-dioxane)$_2$] stabile 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.

Keywords: FT-IR spectroscopy; Metalloporphyrin; Molecular complex; DSC; Thermogravimetry

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 stabile. 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}N–^{15}N, ^{12}C–^{13}C, H–D ^{14}N–^{15}N, ^{12}C–^{13}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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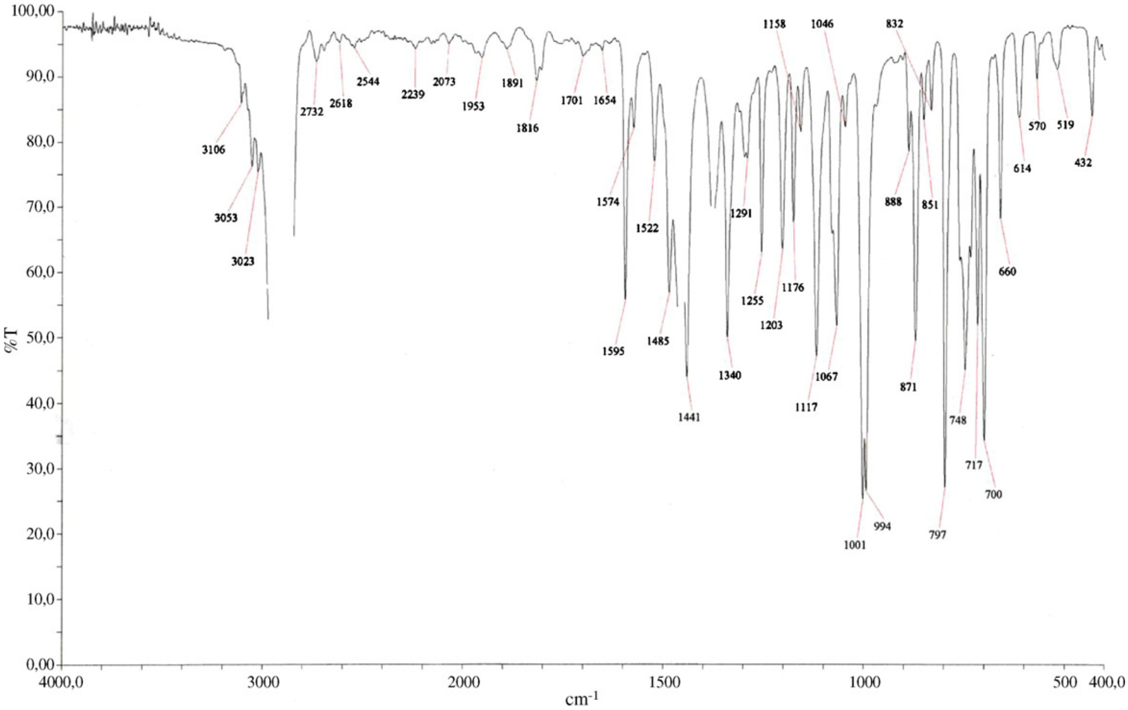


Fig. 1. FT IR spectrum of nujol mulls of [Zn(TPhP)(1,4-dioxane)$_2$] crystalline complex in the 400–4000 cm^{-1} range. Baseline correction was used.

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

The frequencies of 1,4-dioxane for the [Zn(TPhP)(1,4-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}: $\Gamma = 10\ a_g\ (R) + 9\ b_u\ (IR) + 9\ a_u\ (IR) + 8\ b_g\ (R)$
for C_{2v}: $\Gamma = 10\ a_1\ (IR, R) + 9\ a_2\ (R) + 9\ b_1\ (IR, R) + 8\ b_2\ (IR, R)$.

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).

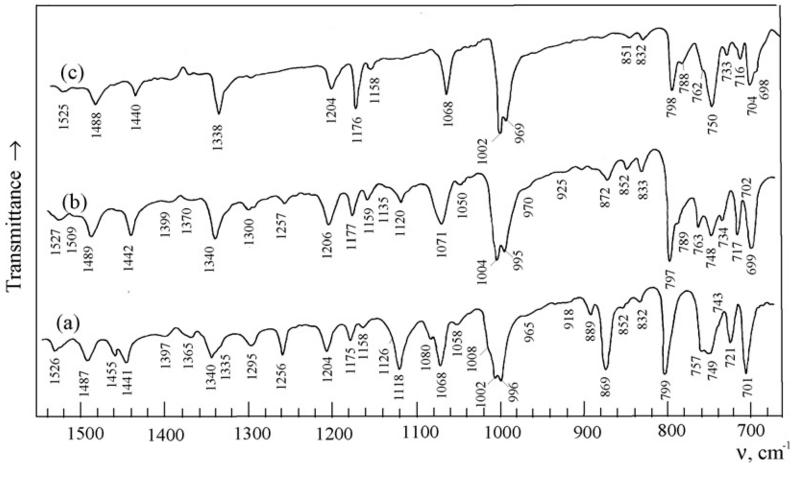


Fig. 2. Dependence of infrared spectra of crystalline films of ZnTPhP on KBr disk on 1,4-dioxane content. Mol.% 1,4-dioxane is 67 (a), 30 (b) and 0 (c).

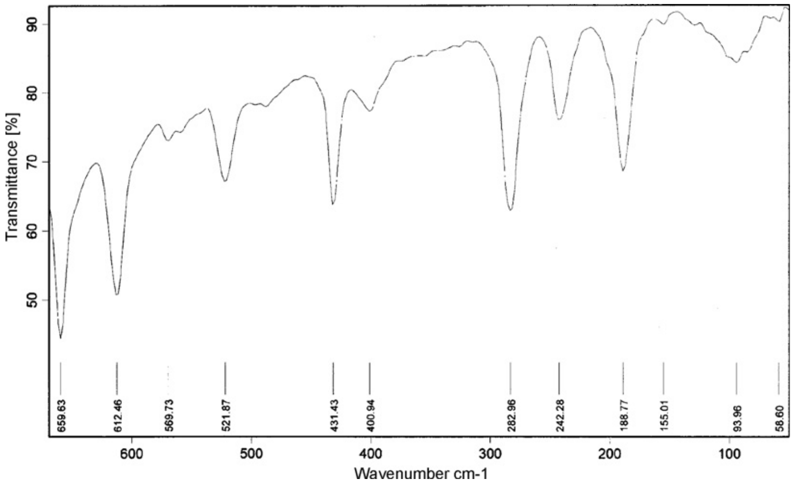


Fig. 3. Far infrared spectrum of [Zn(TPhP)(1,4-dioxane)$_2$] mull.

Table 1
IR data (cm^{-1}) for the free 1,4-dioxane and its molecular complex with ZnTPhP

[Zn(TPhP)(1,4-dioxane)$_2$]. nujol mull	Crystal film of ZnTPhP treated by 1,4-dioxane on CsI and KBr windows	Liquid 1,4-dioxane	
		IR data and assignment according to [8]*	
	2966	2967s	$\nu_{11}(b_u)$
	2925 sh 2918	2921s	$\nu_{20}(a_u)$
	2890	2899w	$\nu_{21}(a_u)$
	2858	2860s	$\nu_{12}(b_u)$
		2760w	$\nu_4 + \nu_{22}(A_u)$
		2695w	$\nu_3 + \nu_{15}(B_u)$
1450 (?)	1455	1446s	$\nu_{13}(b_u)$, $\nu_{22}(a_u)$
	1397	1400w	$\nu_5 + \nu_{19}(B_u)$
	1365	1368m	$\nu_{14}(b_u)$
1340 (?)	1333	1318w	$\nu_{23}(a_u)$
1291,1295	1294	1286 s	$\nu_{24}(a_u)$
1255	1256	1251s	$\nu_{15}(B_u)$
1125sh	1126	1120s	$\nu_{16}(b_u)$
1117	1118		
1078	1080	1081s	$\nu_{25}(a_u)$
1046	1048	1046m	$\nu_{26}(a_u)$
888	889	887s	$\nu_{17}(b_u)$
871	869	874s	$\nu_{27}(a_u)$
614	615	610s	$\nu_{18}(b_u)$
283	284	283m	$\nu_{28}(a_u)$
	276	273m	$\nu_{19}(b_u)$

* Numeration of normal vibrations differs from that described in [8].

The thermochemical investigations showed that chemical composition of the studied complex is Zn(TPhP): 2(1,4-dioxane) and the enthalpy formation estimated by DSC method is 96.0 ± 1.9 kJ mol^{-1}. The formed 1:2 complex is kept in air atmosphere for a long time without changing its composition in agreement with the thermogravimetric data on its stability. No changes were found after IR irradiation during several hours.

To elucidate a nature of the [Zn(TPhP)(1,4-dioxane)$_2$] complex, the far infrared spectra of ZnTPhP and [Zn(TPhP)(1,4-dioxane)$_2$] also have been studied. The results show the absence of the prominent ν(Zn–O) band in the region $\geq$50 cm^{-1} (Fig. 3), although it may be expected that the complex stability is determined by a strong of Zn–O bond. It is likely that the very weak band at 94 cm^{-1} is assigned to translational vibrations of the lattice, probably with admixing of the stretching Zn–O mode. The band found at 189 cm^{-1} is assigned to Zn–N stretching vibration. It is shifted to 197 cm^{-1} in the ZnTPhP spectrum. Previously this band was found at 203 cm^{-1} for the ZnTPhP [10,13]. The band at 242 cm^{-1} is similar to that at 244 cm^{-1} (out-of-plane mode) in the ZnTPhP spectrum. The band at 283 cm^{-1} is assigned to1,4-dioxane mode (Table 1). So the coordination of the solvent molecule by Zn^{2+} ion occurs rather due to weak Zn–O donor–acceptor bonding.

2. Experimental

ZnTPhP was synthesized and purified by chromatography [5]. To remove solvent molecules, the crystal samples were dried

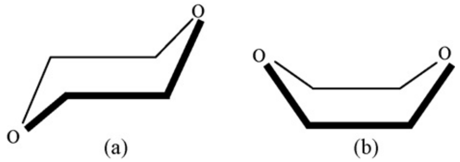
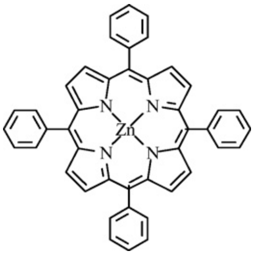


Fig. 4. Scheme of "chair"(a) and "bath"(b) forms of free 1,4-dioxane.

under vacuum at 320–350 K during several days. The electronic absorption spectra agree well with the data published earlier [14].



1,4-Dioxane was purified by column chromatography on activated Al_2O_3 to remove peroxide impurities and then distilled. Presence of the peroxides was checked by reaction with Fe(II) thiocyanate. The water content determined by Karl Fisher titration was found to be less than 0.01%.

The samples of the crystallosolvates of ZnTPhP with 1,4-dioxane were prepared by the ZnTPhP dissolving in excess of 1,4-dioxane. Then the solution was heated up to boiling temperature, and the solvent excess was removed after cooling by flow of air.

The thermochemical investigations were performed using differential scanning calorimeter SETARAM TG-DSC 111 (in nitrogen atmosphere, the reference substance is Pb), Du Pont 2100 Thermal Analysis DSC 910 (in argon atmosphere, the reference substance is In) and thermoanalytical set (in air, the reference substance is Al_2O_3) [6]. As an example, a DSC curve of the crystallosolvate of ZnTPhP with 1,4-dioxane is presented in Fig. 1. To observe the solvent evaporation process at non-isothermal conditions, a heating rate of $0.6\,^{\circ}C\,min^{-1}$ was used.

The IR spectra of the nujol mulls and thin crystalline films in the range from 400 to $4000\,cm^{-1}$ were recorded on a FT-IR spectrometer Perkin-Elmer 2000 and from 50 to $650\,cm^{-1}$ on a FT-IR spectrometer Bruker IFS 66 s. The appropriate thin crystalline films were prepared by evaporation of solvent from the solution of ZnTPhP·1,4-dioxane–CCl_4 on the KBr and CsI plates. The evaporation of the volatile solvent leads to considerable losses of 1,4-dioxane. To compensate these losses, the solid films were treated with the liquid 1,4-dioxane a few times.

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