

CRYSTAL SOLVATES OF TETRAKIS(3,5-DI-*t*-BUTYLPHENYL)-PORPHYRINATES Mn(III), Ni(II) AND Zn(II) WITH PYRIDINE

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The crystal solvates of complexes MP (*P* is the dianion of tetrakis(3,5-di-*t*-butylphenyl)porphin, *M*=Ni(II), Zn(II)) and (Ac)MnP with pyridine have been obtained by isothermal evaporation of corresponding solutions at 35°C. The formation and the decomposition temperatures of crystal solvates and enthalpies of evaporation pyridine molecules from those crystal solvates were received using thermogravimetric method. In addition to that, an influence of the type of metal on the compositions, the energetic and thermal stabilities of the received complexes were analyzed.

Keywords: axial coordination, crystal solvate, molecular complexes, tetrakis(3,5-di-*t*-butylphenyl)porphin, TG

Introduction

It is known that porphyrins are widely used for creation of effective substitutes for blood, artificial coenzymes, catalysts of different processes, photosensibilizers, semiconductors, etc. The general challenge of successful application of porphyrins is an understanding of the mechanisms of intermolecular interaction processes involving them. The ability of metalloporphyrins to bind pyridine axially and form stable crystal solvate structures with it represents a special interest. Study of the axial binding features is useful for understanding the mechanisms of the toxic influence of pyridine and for the creation of the new polyfunctional materials [1–6]. The crystal solvates of porphyrins were investigated only for 30 years (the complete information about this question has been reflected by Byrn *et al.* [7]). However, similar compounds were defined clathrates that do not have strict regular structure and are unstable even at normal conditions. For the first time the ability of porphyrin to create crystal solvates with pyridine was studied in [8–10], where natural porphyrins and tetraphenylporphyrin were employed. Authors have proved that these crystal solvates have constant stoichiometric structure and high stability. Additionally, these works showed many advantages of thermogravimetric method of investigation of crystal solvate structures. In any case, a general problem with the investigation of porphyrins, conditioned by low solubility in the organic solvents (up to 10⁻⁴ mol L⁻¹), retains in this method. Therefore the results presented here are the ones of the thermogravimetric investigations of the crystal solvates of pyridine formed by tetrakis(3,5-di-

t-butylphenyl)porphyrinates zinc(II), nickel(II) and manganese(III) (Fig. 1), which have enough solubility in the pyridine. That allowed to find energetically and thermally stable molecular complexes and analyze the influence of structural factors and a nature of a central ion on investigated properties.

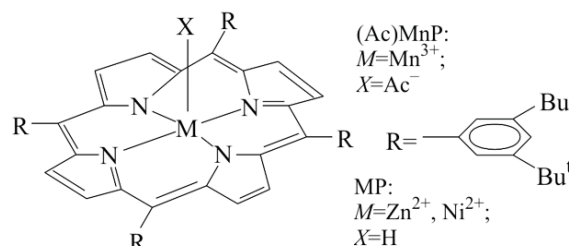


Fig. 1 The molecular structures of tetrakis(3,5-di-*t*-butylphenyl)porphyrinates

Experimental

The synthesis, methods of purification and some H₂P and MP properties (¹H NMR, EPR) were previously published by our group [11]. The synthesis of (Ac)Mn(III) tetrakis(3,5-di-*t*-butylphenyl)porphyrinate were depicted in [12].

The pyridine (Py) used in experiments was a highly purified commercial product. The water content of the solvent was determined by Karl Fischer titration [13] and did not exceed 0.02%. The crystal solvates of metalloporphyrins were prepared by a slow evaporating of their saturated solutions in pyridine at 25–30°C [14].

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Differential thermal and thermogravimetric analysis were performed on the derivatograph 1000D (MOM, Hungary) in an air atmosphere at a heating rate of $2.5^{\circ}\text{C min}^{-1}$ at 15–250°C interval. The sample mass was about 150–200 mg. The enthalpy change in the process of evaporation of crystal solvate ($\Delta_{\text{vap}}H$) was calculated from thermograms according to method presented in [14]. There were two series of experiments for each set of initial substances. In the first set, the samples containing mostly crystals and a little quantities of solution were analyzed. For the second set the samples (crystals+saturate solution) were being kept for not less than 24 h in the vacuum chamber at 30–100°C up till they reached a constant mass. The reproducibility of experiments was achieved by five or more experiments for each set of initial samples. Absence of decomposition processes of porphyrin molecules was proved by spectrophotometric experiments carried out after thermogravimetric analysis.

Results and discussion

Typical derivatograms of samples and the results of thermogravimetric analysis are presented on the Fig. 2, and in Table 1 jointly with literature data for MTPP.

All samples from the first series of experiments that contained MP exhibited two consecutive stages that were reflected in derivatograms in the forms of endothermic peaks on the DTA curve. These stages were followed by the decrease in mass (Fig. 2a). That mass decrease on the first low temperature stage is proportional to the mass of saturated solution. Also, the pyridine $\Delta_{\text{vap}}H$ value makes a good agreement with evaporation enthalpy of clear solvent in suitable tem-

Table 1 Physicochemical characteristics of MP and MTPP crystal solvates with pyridine

Composition	MP- <i>n</i> Py	T_n	$\Delta_{\text{vap}}H$
(Ac)MnP	1:2	122	53.5
	1:1	140	19.2
NiP	1:1	115	21.2
ZnP	1:1	1478	50.4
(Ac)MnTPP ^a	1:2	135	73.2
	1:1	145	26.6
NiTPP ^a		does not form	
ZnTPP ^a	1:1	190	86.4

T_n – the temperature of the decomposition start, °C;
 $\Delta_{\text{vap}}H$ – evaporation enthalpy of pyridine from crystal solvates, ± 0.8 – 1.5 kJ mol^{-1} ; ^adata from the literature

perature interval [14]. Therefore the existence of this stage depends on the extraction of residual free solvent in steady solvate structures [15]. The mass decrease on the second stage depends on the mass of pyridine molecules combined in a special way. That allows calculating the composition of steady MP crystal solvates, which was determined to be 1:1 for NiP and ZnP crystal solvates and 1:2 for (Ac)MnP crystal solvate. The second stage of the mass decrease process for the sample with (Ac)MnP is also double-staged. That signifies towards consecutive extraction of two pyridine's molecules combined non-equivalently.

Only one stage of decreasing mass is fixed at heating the samples of the second set, which is observed in the field of high temperatures (Fig. 2b). That corresponds to the second stage that is experienced by the first set of samples. It is referred to an extraction of pyridine molecules combined in a special way. Subsequent heating of samples of both sets up to the temperature of metalloporphyrin decomposition (200–380°C)

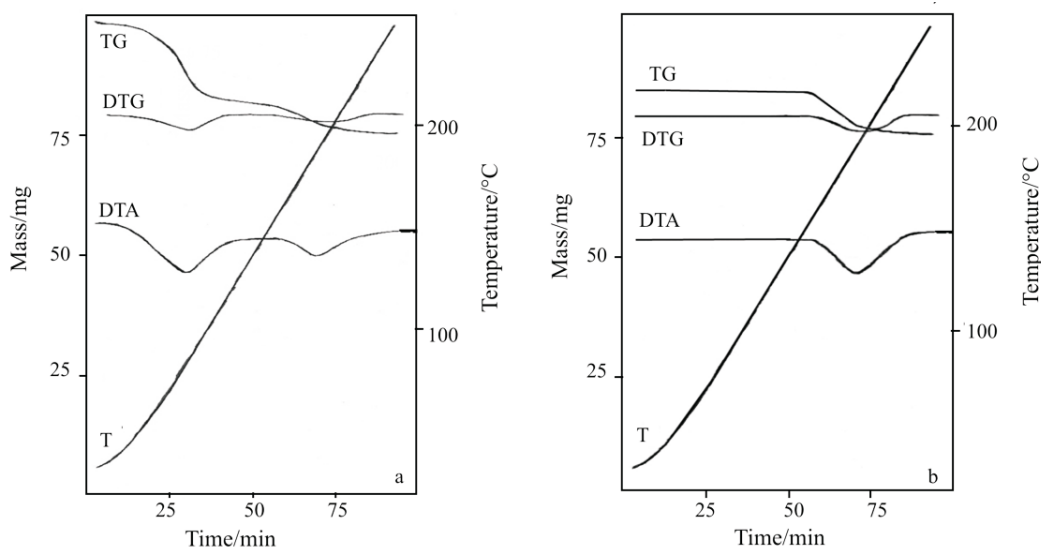


Fig. 2 TG, DTG, DTA and T curves of ZnP·Py crystal solvate of the a – first and b – the second groups

did not lead to the change in TG curve and appearance of the peaks on DTA and DTG curves.

According to the results shown in Table 1, NiP has a minimal thermal and energetic stability among investigated crystal solvates. Zinc porphyrinate is more stable thermally; on the other hand manganese porphyrinate is more stable energetically. The last one forms a crystal solvate with two pyridine molecules. Such composition is typical for molecular complexes formed by metalloporphyrins with triple-charged metallic ions and electron-donating ligands [16–20]. It is interesting that the second pyridine molecule in (Ac)MnP-2Py crystal solvate is bound to (Ac)MnP almost three times as stronger as the first one. It can be explained by fact that the weaker bounded pyridine molecule gets into 6th coordinating site of Mn. The formation of the strong bond from this site is difficult because metal ion is shifted out of the plane of porphyrin macrocycle structure by acid ligand. The addition of the second pyridine molecule leads to the substitution of acid ligand into external coordinating sphere of (Ac)MnP. The analogous mechanism of (Ac)MnTPP-2Py crystal solvates formation was described in earlier [21] and can be presented by the following model below.

It is necessary to note that the high ability of porphyrin complexes of manganese to bind electron-donor molecules axially is a typical effect. It was described in works [19, 22, 23].

The crystal solvate of zinc porphyrinate that includes one pyridine molecule only is as energetically stable as manganese crystal solvate. The five-coordinated state of Zn that is a part of metalloporphyrin is a fairly typical phenomenon [24]. But a six-coordinated state has been discussed in one work only. It is interesting, that in this case axial ligands contain oxygen [25]. Substitution of zinc by nickel in ZnP-Py leads to essential decrease of crystal solvate energetic stability that, most likely, can be explained by decreased ionic radii of Ni²⁺ and Zn²⁺ equal to 0.78 and 0.83 Å, accordingly. It is necessary to explain that the sizes of metal ions and porphyrin cavity play an important role in formation of axial complexes. Their relation to each other increases the stability of corresponding porphyrinate and decreases the energy and length of M-N_{py} axial bond.

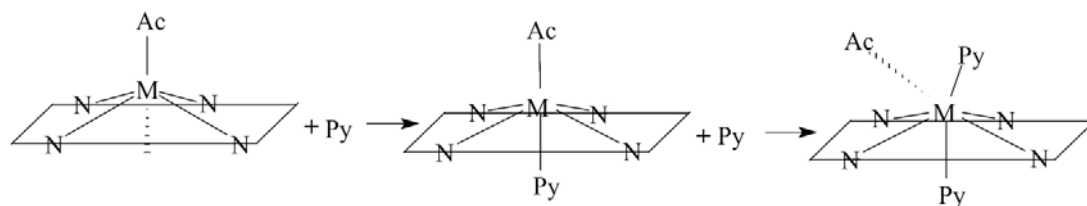
Comparative analysis of data obtained for MP crystal solvates and their unsubstituted ana-

logues (MTTP) (Table 1) allowed to define the influence of alkyl substitution on composition and energetic characteristics of crystal solvates. It was found, that introducing *t*-butyl substitutes in the case of (Ac)MnTPP and ZnTPP does not influence the composition of crystal solvates created; although, it decreases their thermal and energetic stability (Table 1). Decreasing the energetic stability of crystal solvates due to introduction of alkyl substitutes in phenyl groups of H₂TPP can be explained by:

- electronic effects of substitutes – the displacement of electronic density towards the macrocycle due to positive induction effect of *t*-butyl substitutes. This effect leads to increase in strength of metal bonds with nitrogen atoms from pyrrol group and weakening the ones with nitrogen atom from pyridine molecule
- steric effects of large substitutes, consisting of loosening a crystal lattice

Some works [26–29] can serve as a confirmation of substitutes' steric effect. For example, it has been shown in article [26] by the method of photoelectron spectroscopy that distances between crystallographic planes in H₂P, CuP, NiP and ZnP crystals are close to 7.0 Å, that is much larger than the ones for ligand and tetraphenylporphyrinates [27, 28]. Steric influence of *t*-butyl substitutes is discussed by Golder *et al.* in the investigation of nickel(II) *meso*-tetrakis(3,5-di-*t*-butyl-4-hydroxyphenyl)porphyrinate [29]. They pointed out the decreasing density (ρ) of the unit cell in solid porphyrin samples, that have triclinic system, up to 1.01 g cm⁻³ and the increase of distances between the nearest metal atoms (M...M) up to 10.7 Å (according to typical parameters for complexes of tetraphenylporphyrin M...M is about 8 Å and $\rho=1.29-1.48$ g cm⁻³).

At the same time the introduction of *t*-butyl substitutes into NiTPP helps to form stable crystal solvates with pyridine. But if NiTPP does not form a crystal solvate with pyridine, then $\Delta_{\text{vap}}H$ for NiP-Py is 21.2 kJ mol⁻¹. So, introducing *t*-butyl substitutes makes porphyrinate act as coordinately unsaturated complex. It is known, that most of nickel porphyrinates are coordinately saturate and do not have the possibility to additionally bind electron-donating molecules. On another hand, the possibility of weak binding of pyridine by NiTPP is mentioned in work [30]. According to that the logarithms of constants of axial binding process of



pyridine by NiTPP in chloroform and benzene are 2.19–3.01 and 1.85–3.15, respectively (the deviations of $\lg K$ depend on the method of defining the constants). The Ni(II) complexes of the natural porphyrins form stable solvates with pyridine [10]. Formation of bi-pyridine nickel porphyrinate NiTPP(CN)₄(Py)₂ was established in work [31]. On the other hand the results of calorimetric measurements obtained in article [32] show the binding saturation of NiP complex. It is interesting that the main reasons causing the weak binding unsaturation of the Ni²⁺ ions in NiP are the effects of alkyl substitution just like in the case of the decrease of Mn and Zn crystal solvates stability. This seeming contradiction is explained by the need to take into account a presence of the opposite π -dative Ni \rightarrow N_{py} bond, that is absent in (Ac)MnP and ZnP. As a result, the opposite π -dative interaction of nickel ion with macrocycle in NiP–Py complex weakens due to +I-induction effect of *t*-butyl substitutes. On the other hand the steric factor leads to distortion of the plane structure causing the metal to leave the coordinating cavity of chromophore. Both of these factors lead to weakening of metal cation and porphyrin anion interaction and increase of the binding unsaturation of cation.

So, in the work described it was established that the complexes of tetrakis(3,5-di-*t*-butylphenyl)porphin with Ni²⁺, Zn²⁺ and Mn³⁺ form stable crystal solvate structures with pyridine. The energetic stability of those complexes was found to increase in a row of NiP·Py, ZnP·Py, (Ac)MnP·2Py. Therefore, manganeseporphyrinate exhibited the strongest ability of additional coordination. It was also determined that the compositions together with energetic and thermal stabilities of crystal solvates depend on the structure of porphyrin macrocycle and electronic configuration of the central metal ion. In addition to that +I-induction and steric effects of *t*-butyl substitutes in porphyrins were found to influence the ability of metalloporphyrins to form a pyridine solvate depending on the nature of the metal ion (considering the presence of direct or inverse π -donation bonds). In the case of nickelporphyrinate, the introduction of *t*-butyl substitutes considerably increased the coordination non-saturation of Ni²⁺, which was considered to be uncommon. It is important that in the process of formation and stabilization of crystal solvates the sizes of metal ions corresponded to the ones of a porphyrin cavity. With the higher degree of such correspondence, the stability of crystal solvate structures decreased. The dependences described above present the possibility of controlled management of inter- and intramolecular interactions in given compounds, that could be employed in nanomolecular technologies [33, 34] and chemical analysis [35].

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