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Crystal Solvates of Porphyrins and Metalloporphyrins

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Abstract—The published data on the crystal solvates with nonpolar aromatic and electron-donor compounds obtained using different research methods as well as our own experimental results obtained by thermogravimetric analysis of the porphyrins and metalloporphyrins of natural and synthetic origin are generalized. The influence of the molecular structure of the porphyrins and metalloporphyrins on the composition, structural parameters, thermal and energy stability of crystal solvates formed through specific σ-and π-complexes with molecular ligands are considered.

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State and properties of porphyrins and metalloporphyrins in a solution, solid phase and biostructure are determined largely by the features of interactions between the particles. The large size of the hydrocarbon frame, extended π-bond system, the presence of polar heteroatomic groups in the complex and of the residual positive charge on the complex forming metal atom create the conditions for universal and specific donor-acceptor interactions (of σ- and π–π-type) of the porphyrin and, in particular, metalloporphyrin, with nonpolar (including aromatic) and polar molecules or fragments [1–3]. Often due to the specific interactions the molecular complexes are stable both in solution and as the crystal solvates. X-ray diffraction and thermogravimetric analysis of crystal solvates of porphyrins and metalloporphyrins provide valuable information not only on the state of the compound in solid phase, but also on the features of its solvation in a solution. The availability of data on specific interactions of the porphyrins and metalloporphyrins with the solvent molecules of different nature provides a possibility to overcome many problems at interpreting the results of spectral, thermochemical, and other similar research. Often these problems are caused by incorrect choice of the reference oligopyrrole–"standard" solvent system: in such a system the studied compounds should be solvated only through universal interactions. In calorimetric and spectroscopic studies as "standard" solvents for porphyrins and metalloporphyrins commonly benzene or its alkyl derivatives (toluene, xylenes) are used. However, as we show later, this choice is correct not in all cases and can lead to incorrect estimates of the oligopyrrole reactivity, since the formation of specific solvates substantially affects the properties of dissolved compounds and their solutions. No less problematic is the consideration of the data on the solubility of oligopyrroles in organic solvents obtained by isothermal saturation, because often at the reaching the *solution–bottom phase* equilibrium, the composition of the latter is changed due to crystallization from solution of not a compound itself, but its crystal solvate [4]. In addition, the data on the composition and stability of the crystal solvates are necessary at selecting conditions for obtaining high-purity samples of porphyrins.

Results of X-ray diffraction and thermogravimetric analysis of the porphyrin and metalloporphyrin crystal solvates accumulated to date give a knowledge on the existence of stable solvated structures in solution based on the characteristics of interaction of species in the solid phase. The crystal solvates precipitated from a solution commonly include the most strongly bound solvent molecules, but loose the rest of the solvent shell. Therefore, the composition of crystal solvates makes it possible to judge on the existence of specific solvate complexes in solution.

Along with the structural factors ensuring the conditions for specific interactions, the crystal packing of compounds of this class can favor formation of the porphyrin and metalloporphyrin crystal solvates. The interplanar distances and volumes of cavities between adjacent layers of monomolecular oligopyrrole in a crystal should be large enough to create conditions for free location not only of small particles (inorganic ions, solvent molecules), but such large molecules like fullerenes, etc. In many cases, the specific molecular complexes with solvent (solvates) stable in the solid state under normal conditions constitute the elementary fragments of crystals of the porphyrin and metalloporphyrin.

Specific features of the porphyrin and the metalloporphyrin structures provide conditions for the formation of two types of molecular complexes: (1) σ-complexes, in which molecular ligands are bound by the metal ion through directed donor-acceptor interaction (axial coordination) and by the atoms of the acid–base groups >NH and ≡N at the reaction center or fragments of the polar substituents of the porphyrin; (2) π–π-complexes, formed by multicenter stacking interactions of aromatic π-systems of the ligand and the porphyrin.

Overview of XRD data allows a classification of the porphyrin and metalloporphyrin crystal solvates with the molecules of liquid or gaseous substances as two main types:

(1) Unstable crystal solvates that contain molecules of “residual” solvent in the cavities of the crystal lattice, not bound by the specific interactions with the porphyrin. As a rule, such solvates are not reproducible and their stoichiometric composition is not expressed by an integer value. The solvent is easily removed from the crystal solvates even under “normal” conditions (T = 290–300 K, p = 1 atm) or at minor deviations from them (heating, evacuation). To these crystal solvates the term “clathrate” is the most applicable [5].

(2) Stable crystal solvates formed by specific σ- and π–π-complexes of the porphyrin or metalloporphyrin, which are characterized by a reproducible composition and integer value of the porphyrin – molecular ligand molar ratio. Removal of the solvent molecules or other volatile substances from such a crystal requires considerable energy expenditure and is possible only at heating to relatively high temperatures (even under conditions of reduced pressure).

Note that scientific literature contains virtually no data on the XRD of the crystal solvates formed by the axial complexes of metalloporphyrin, in contrast to the crystal solvates formed by the molecular π–π-complexes of the porphyrin and metalloporphyrin. The first information (NMR, ESR, XRD) on the π–π-complexes of porphyrins appeared in nineteen eighties–nineties [6–11]. Study of π–π-complexes is of particular interest for revealing the mechanisms of the most important biological processes, like inhibition of cytochromes and other chromoproteines by toxic aromatic compounds (benzene, its derivatives, etc.); the transport and accumulation of drugs, hormones, and neurotransmitters; the adsorption and catalysis, etc. So, by the example of the model structures of cytochromes [12] using circular dichroism and NMR spectroscopy it has been shown that the “alien” to the body aromatic lipophilic molecules compete successfully with aromatic radicals of amino acid residues of peptides in stacking interactions with metalloporphyrin, which leads to disruption of the native structure and inhibits the biological functionality of the chromoproteins. The similarity in the structures of the *plane–plane* type for π–π-complexes of porphyrins in natural conditions and in solution was confirmed in [13–15]. It was found that the stacking interaction with trinitrobenzene, a strong π-acceptor, hinders the coordination of O_2 by the metalloporphyrin. Strong stacking interactions of the Mn(III) porphyrinates with dimethylaniline and hexamethylbenzene [13] and the Mn(III), Fe(III), Co(III), Ni(II), Cu(II), and Ag(II) porphyrinates with caffeine have been proved in [7]. ESR data confirmed the existence in solutions of the π–π-complexes of 1:1 and 1:2 composition of the Co(II) aryltetraphenylporphyrinates with strong π-acceptors [6], Co(II) tetra-*p*-tolylporphyrinate with various aromatic π-acceptor or π donor of 1:1 composition [10]. The published information on the role of metal in the metalloporphyrin π-stacking with aromatic ligands is very contradictory. Fulton et al. [9, 10] suggest that in the π–π-complex of trinitrobenzene with Co(II) tetratolylporphyrinate the metal ion is not involved in the process of molecular complexation. In [13, 16–18] while considering the results of the XRD of π–π-complexes of Zn(II), Cr(II), and Mn(III) tetraphenylporphyrinates with nitrobenzene and toluene, the opposite conclusion were reached. In the more recent studies [19–21] also was noted that the nitro derivatives of simple aromatic compounds form with metalloporphyrin unusual centrosymmetric structures in which the solvent molecule is located above the metal, so its participation in the formation of π–π-complex is possible.

Fairly complete data on the XRD of crystal solvates of the porphyrin and metalloporphyrin aryl derivatives were compiled in the review [22], which presents the quantitative characteristics of molecular packing of over two hundred crystal solvates, many of clathrates. However, this review does not include the data on the intermolecular *guest–host* distances, making it difficult to assess the stability of the solvates. It should be clarified that a crystal solvate formed through the porphyrin–molecular ligand stacking interaction is assigned to the second type (stable crystal solvate) based on XRD analysis when the shortest distance between contacting molecules is less than 3.5 Å, which assumes the overlap of their π systems [23]. More informative in this sense are the data on the XRD of the crystal solvates of tetraphenylporphin with bisbenzaldehyde [24], bis(*m*-xylene) [25], anthracene, phenanthrene, and pyrene [26]. Based on the fact that the distance between the porphyrin and the guest molecules are 3.26–3.50 Å, a possibility of specific stacking interactions in such solvates was assumed.

Crystal solvates of tetraphenylporphin (H_2TPP) and its metal complexes MTPP, M = Mn(II), Fe(III), Co(II), Cu(II), and Zn(II) with fullerenes [27–30] are characterized by centrosymmetric arrangement of the fullerene over the reaction cavity of the macrocycle with short (on 3.3 Å) N···C distances, therefore it is assumed that the *host–guest* interactions are of the van der Waals nature. Such complexes are considered as supramolecular matrices that can rigidly fix the fullerene molecules and reduce their rotation [31].

In [32] the features are discussed of crystal packing in the crystal solvates of *para*-HO-, Cl-, F-phenyl-substituted ZnTPP. The data on *p*-hydroxy-substituted H_2TPP and its tetra(3,5-di-*t*-butyl)-substituted analog H_2T(3,5-di-*t*-BuP)P were published in [33–35]. The minimum distance between the porphyrin plane and fullerene is 2.69–2.88 Å. The introduction of a large *guest* molecule in the porphyrin crystal lattice affects insignificantly both the type of crystal packing and also the distance between the monolayers of the *host* molecules.

As noted above, the results of XRD analysis allow judging on the stability of crystal solvates only indirectly, from the intermolecular distances. An informative and accessible method for studying the the porphyrin and metalloporphyrin crystal solvates with the molecules of organic solvents and other volatile substances is thermogravimetric analysis, which permits not only studying the composition and thermal stability of the crystal solvates, but also an estimation of the energy characterizing interspecies *guest–host* interactions proceeding from the enthalpies of evaporation of volatile component in the process of the solvate thermal dissociation [36–38]. Using this approach, an extensive database of physical and chemical properties of crystal solvates of natural and synthetic porphyrins and metalloporphyrins with nonpolar aromatic and electron-donating solvents [39–63] was collected. The main results are shown in Tables 1–3. The analysis of the data obtained with respect to the characteristics of the molecular structure of the porphyrin, metalloporphyrin and the solvent resulted in the following general rules:

(1) The ability to form stable crystal solvates is a general property of the porphyrin and metalloporphyrin from both synthetic and natural sources.

(2) Metalloporphyrins form a more stable crystal solvates than porphyrin ligands.

(3) Stable crystal solvates can be formed by σ-complexes of the porphyrin and metalloporphyrin with electron-donor and electron-acceptor solvents (through axial coordination with the metal or interactions with polar substituents) and π–π-complexes with aromatic solvents.

(4) The increase in the electron density in the macrocycle (due to electronic effects of substituents and/or dative metal–ligand π-bonds) promotes the formation of π–π-complexes with π-acceptors, the macrocyclic ligand in their composition acts as a donor of π-electron density (and vice versa).

Note that the generally accepted method of purification of porphyrins from the impurities of the organic solvent is keeping in a vacuum at 60–100ºC of solid samples isolated by recrystallization from solutions, which not in all cases leads to the desired result. Thus, in [39–42, 48, 53] to investigate the crystal solvates $H_2T(3,5\text{-di-}t\text{-BuC}_6H_3)P$ and $MT(3,5\text{-di-}t\text{-BuC}_6H_3)P$ two series of samples were analyzed (Figure 1): (1) the heterophase systems containing crystal solvates and the residual saturated solution, (2) crystalline samples dried additionally in a vacuum pistol at heating. The thermograms of samples of the first series (Fig. 1a) include a low-temperature phase of the weight loss with an endothermic peak on the DTA curve due to the removal of residual solvent that is not bonded by the porphyrin to a stable complex.

Table 1. Composition, temperature of the degradation beginning (t_{beg}) and vaporization enthalpy ($\Delta_{vap}H$) of the molecular ligands at the thermal dissociation of the crystal solvate by the data of thermogravimetric analysis [39–63]

Solvate[a]	Composition	t_{beg}, °C	$\Delta_{vap}H$, kJ mol^{-1} [b]	Solvate[a]	Composition	t_{beg}, °C	$\Delta_{vap}H$, kJ mol^{-1} [b]
$H_2GP–C_6H_6$	1:1	337	82.3	ZnTPP–*o*-xylene	1:2	75	151.3
$H_2PP–C_6H_6$	1:1	39	41.0	ZnTPP–*m*-xylene	1:2	68	88.0
$H_2DP–C_6H_6$	1:1	42	33.6	ZnTPP–*p*-xylene	1:0.5	118	81.3
$H_2MP–C_6H_6$	1:1	66	30.4	(AcO)MnTPP–$C_6H_5CH_3$	1:1	75	182.0
H_2GP–Py	1:1	132	60.9	(AcO)MnTPP–*o*-xylene	1:2 1:1	70 80	82.2 31.6
H_2PP–Py	1:1	84	40.5	(AcO)MnTPP–*p*-xylene	1:1	68	74.6
H_2DP–Py	1:1	76	39.0	(AcO)MnTPP–*m*-xylene	1:1	56	69.8
H_2MP–Py	1:1	70	24.9	ZnTPTBP–Py	1:1	130	73.3
$H_2T(3,5\text{-}t\text{-}Bu_2\text{-}4\text{-}OHPh)P$–Py	1:4	58	53.3	ZnTBP–Py	1:1	150	83.1
H_2T(*o*-BrPh)P–Py	1:1	100	–	$ZnT(3,5\text{-}t\text{-}Bu_2\text{-}4\text{-}OHPp)P$–Py	1:5 1:1	110 146	91.6 79.1
$ZnT(3,5\text{-}t\text{-}Bu_2\text{-}4\text{-}OHPh)P–C_6H_6$	1:2	76	73.2	ZnGP–Py	1:2	143	128.0
$ZnTBP–C_6H_6$	1:2	76	150.2	ZnDP–Py	1:1	128	95.0
$ZnTPTBP–C_6H_6$	1:2	83	141.4	ZnMP–Py	1:1	120	68.2
$ZnGP–C_6H_6$	1:2 1:1	50 126	40.0 97.3	ZnPP–Py	1:1	108	63.4
$ZnDP–C_6H_6$	1:1	73	63.2	NiGP–Py	1:1	136	99.2
$ZnMP–C_6H_6$	1:1	62	42.2	NiPP–Py	1:1	103	74.8
$ZnPP–C_6H_6$	1:1	49	18.3	NiDP–Py	1:1	78	55.7
$NiGP–C_6H_6$	1:2 1:1	62 121	50.0 90.0	NiMP–Py	1:1	72	36.9
$NiDP–C_6H_6$	1:1	32	26.0	$(Cl)FePP–C_6H_6$	1:2 1:1	104 118	90.1 108.4
$NiMP–C_6H_6$	1:1	42	21.9	$ZnTPP–C_6H_5CH_3$	1:2	51	72.0

[a] GP is hematoporphyrin, DP is deuteroporphyrin, MP is mesoporphyrin, TBP is tetrabenzopophyrin, TPTBP is tetraphenyltetrabenzoporphyrin, TPP is tetraporphyrin. [b] Hereinafter $\Delta_{vap}H = \pm(0.8–1.5)$ kJ mol^{-1}.

The derivatograms of the second series of samples (Fig. 1b) do not include the low-temperature phase [55], but at higher temperatures the curves of heating samples of the first and second series are similar. If the crystalline sample is a stable porphyrin–solvent solvate complex, the derivatogram includes an endothermic stage of the weight loss with the porphyrin–solvent molar ratio expressed by an integer value, and usually with a relatively high $\Delta_{vap}H$ value of removing the solvent from the crystal [61].

The presence of thermogravimetric data for a wide range of porphyrins and metalloporphyrins allows evaluation of the impact of structural factors on the ability of macrocyclic tetrapyrrole to form stable crystal solvate with an aromatic ligand. As noted above, depending on the ratio of π-donor ability of aromatic systems of the partners, porphyrins and metalloporphyrins can act in specific π–π-complexes either as a π-donor or as a π-acceptor with respect to the molecules of aromatic ligands [19]. In the π–π-complexes with a strong π-electron acceptor (nitrobenzene, trinitrobenzene, etc.) the porphyrin π-system is a donor of the π-electron density [19–21]. When the difference in the π-donor properties of the macrocyclic compound aromatic system and low molecular weight ligand (benzene, toluene, and xylenes) is insignificant, the energy of the stacking interactions and stability of the crystal solvate are very sensitive to electronic effects of peripheral substituents and features of the M ↔ P coordinating interaction. Thus, reducing the electron density in the porphyrin macrocycle by the electron +*I*-effects of β-substituents and/or π-dative M–L interaction is accompanied by a decrease in thermal and energy stability of the crystal solvates with benzene and its alkyl derivatives in the following

Table 2. Temperature of the degradation beginning (t_{beg}) and thermal dissociation entalpy ($\Delta_{vap}H$) of the crystal solvates $H_2T(3,5\text{-di-}t\text{-}BuC_6H_3)P$, H_2TPP and their metal complexes with benzene [60, 61, 63]

Solvate	Process	t_{beg}, °C	$\Delta_{vap}H$, kJ mol^{-1}
	$H_2P = H_2T(3,5\text{-}t\text{-}Bu_2Ph)P$, $MP = MT(3,5\text{-}t\text{-}Bu_2Ph)P$		
$H_2P–C_6H_6$	$H_2P·C_6H_6 \rightarrow H_2P + C_6H_6$	53	28.5
$CuP–C_6H_6$	$CuP·2C_6H_6 \rightarrow CuP·C_6H_6 + C_6H_6$	60	27.4
	$CuP·C_6H_6 \rightarrow CuP + C_6H_6$	85	46.6
$AgP–C_6H_6$	$AgP·2C_6H_6 \rightarrow AgP·C_6H_6 + C_6H_6$	60	44.0
	$AgP·C_6H_6 \rightarrow AgP + C_6H_6$	85	19.1
$NiP–C_6H_6$	$NiP·C_6H_6 \rightarrow NiP + C_6H_6$	120	29.6
$ZnP–C_6H_6$	$ZnP·C_6H_6 \rightarrow ZnP + C_6H_6$	66	42.8
$CdP–C_6H_6$	$CdP·C_6H_6 \rightarrow CdP + C_6H_6$	152	14.7
$PdP–C_6H_6$	$PdP·C_6H_6 \rightarrow PdP + C_6H_6$	99	3.7
	MP = MTPP		
$ZnP–C_6H_6$	$ZnP·C_6H_6 \rightarrow ZnP + C_6H_6$	60	155.5
$(AcO)MnP–C_6H_6$	$(AcO)MnP·2C_6H_6 \rightarrow (AcO)MnP·C_6H_6 + C_6H_6$	65	230.5
	$(AcO)MnP·C_6H_6 \rightarrow (AcO)MnP + C_6H_6$	130	65.5

series of synthetic and natural (blood group) porphyrins and metalloporphyrins: MGP > MDP > MMP > MPP; $H_2GP > H_2DP > H_2MP > H_2PP$; (AcO)Mn(III)TPP, (AcO)Cr(III)TPP > ZnTPP [39].

Experimental data [39–63] in Table 1, allow us the estimation of the influence of electronic and steric effects of alkyl and pseudo-alkyl substituents in the phenyl fragments of the tetraphenylporphin derivatives. The ligands $H_2T(3,5\text{-di-}t\text{-}Bu\text{-}4\text{-}OHC_6H_2)P$ and $H_2T(4\text{-}BrC_6H_4)P$ form with pyridine the complexes of 1:4 and 1:1 composition, respectively. In the first case, the complex is formed through the donor–acceptor σ-bonds of the OH protons with pyridine nitrogen, in the second through the >NH···Py hydrogen bond. In contrast to H_2TPP, the ligands of blood group and $H_2T(3,5\text{-di-}t\text{-}BuC_6H_3)P$ form relatively stable 1:1 complexes with benzene (Table 2). The formation of π–π-complexes is not characteristic of $MT(3,5\text{-di-}t\text{-}BuC_6H_3)P$, where M = Mn(III) and Hg(II), unlike the corresponding Zn(II), Cd(II), Co(II), Ni(II), and Pd(II) porphyrinates that form relatively stable crystal solvates with one molecule of benzene, and Cu(II) and Ag(II) porphyrinates, forming with benzene the solvates of $MP·2C_6H_6$ composition. Thermal and energy stability of the solvates $MP·nC_6H_6$ fall to the ranges 48–152ºC and 3.7–151.3 kJ mol^{-1}, respectively. The minimum value of $\Delta_{vap}H$ of benzene was observed for $PdP·C_6H_6$. Among the crystal solvates listed in Table 2 the highest temperature of the degradation beginning (t_{beg}) have $CdT(3,5\text{-di-}t\text{-}BuC_6H_3)P·C_6H_6$, $NiT(3,5\text{-di-}t\text{-}BuC_6H_3)P·C_6H_6$, and (AcO) MnTPP·$C_6H_6$. In general, in terms of numbers and the total energy of specifically bound molecules, a high complexing ability with respect to benzene show CuT (3,5-di-t-BuC_6H_3)P and $AgT(3,5\text{-di-}t\text{-}BuC_6H_3)P$, (AcO)MnTPP, binding in the crystal solvate two unequal by energy C_6H_6 molecules.

Table 3. Temperature of the degradation beginning (t_{beg}) and thermal dissociation entalpy ($\Delta_{vap}H$) of the crystal solvates $H_2T(3,5\text{-di-}t\text{-}BuC_6H_3)P$, H_2TPP and $MT(3,5\text{-di-}t\text{-}BuC_6H_3)P$ with pyridine [60, 61, 67–70]

Solvate	t_{beg}, °C	$\Delta_{vap}H$, kJ mol^{-1}
$(AcO)MnT(3,5\text{-}t\text{-}Bu_2Ph)P·2Py$	122	63.5
	140	39.2
(AcO)MnTPP·2Py	135	73.2
	145	26.6
CoTPP·Py	90	50.3
$ZnT(3,5\text{-}t\text{-}Bu_2Ph)P·Py$	148	50.4
ZnTPP·Py	190	86.4
$CdT(3,5\text{-}t\text{-}Bu_2Ph)P·Py$	177	47.3
CdTPP·Py	162	68.2
$NiT(3,5\text{-}t\text{-}Bu_2Ph)P·Py$	115	21.2
$CuT(3,5\text{-}t\text{-}Bu_2Ph)P·Py$	160	50.2
$HgT(3,5\text{-}t\text{-}Bu_2Ph)P·Py$	184	59.3
$AgT(3,5\text{-}t\text{-}Bu_2Ph)P·Py$	142	51.9
$PdT(3,5\text{-}t\text{-}Bu_2Ph)P·Py$	130	33.4
$H_2TPP·Py$	–	1.3

Energetic stability of $MT(3,5\text{-di-}t\text{-}BuC_6H_3)P$ solvates with the aromatic solvent is reduced in parallel with the growth of the ionic radius of complex forming

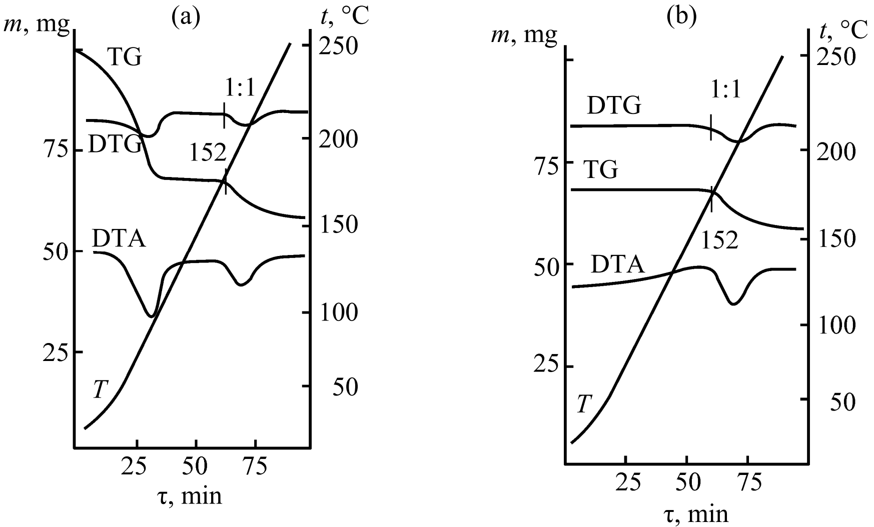


Fig. 1. Derivatogram of the crystal solvate CdT(3,5-di-*t*-BuC$_6$H$_3$)P–C$_6$H$_6$ (a) before and (b) after keeping in a vacuum. TG is thermogravimetry, DTG is differential thermogravimetry, DTA is differential thermal analysis, *T* is temperature.

metal in the subgroups of the periodic system: Zn(II) > Cd(II) >> Hg(II); Cu(II) > Ag(II); Ni(II) >> Pd(II). Obviously, the efficiency of π–π-interactions of the *plane–plane* type is affected appreciably by the steric factors arising at the displacement of the metal ion from the coordination cavity of the porphyrin macrocycle [64, 65], which increases with the radius of the complex forming ion.

Computer simulation of the π–π-complexes MT(3,5-di-*t*-BuC$_6$H$_3$)P, M = Co(II), Cu(II), Ni(II), Zn (II), Cd(II) with benzene in the framework of MOPS algorithm [66] showed similarity of their structures which includes a typical parallel arrangement of the benzene ring plane above the plane of the porphyrin (Fig. 2). The center of the benzene ring is shifted relatively to the center of the porphyrin and is located above the pyrrole nitrogen atom.

The results of thermogravimetric analysis of crystalline samples of σ-complexes with pyridine formed by H$_2$TPP, H$_2$T(3,5-di-*t*-BuC$_6$H$_3$)P and their metal complexes [67–70] are listed in Table 3, Fig. 3 shows a typical derivatogram.

The ligand H$_2$T(3,5-di-*t*-BuC$_6$H$_3$)P does not form pyridinium salts. Its metal complexes, except manganese porphyrinate, form complexes with one molecule of pyridine. Energy and thermal stability of crystal solvates are different: the values of $\Delta_{vap}H$ and t_{beg} vary in the ranges of 21–64 kJ mol^{-1} and 115–184°C, respectively. The maximum values of $\Delta_{vap}H$ and t_{beg} shows HgT(3,5-di-*t*-BuC$_6$H$_3$)P·Py, minimum belongs to NiT(3,5-di-*t*-BuC$_6$H$_3$)P·Py. For the majority of metalloporphyrins, except for Mn(III) porphyrinate, a parallel change is observed in the values of $\Delta_{vap}H$ and second ionization potentials of the complex forming metal in the subgroups and periods of the periodic system [67–70]. In the crystal solvates (AcO)MnT(3,5-di-*t*-BuC$_6$H$_3$)P·2Py, two pyridine molecules are not energetically equivalent. Similar properties are characteristic of the crystal solvates (AcO)MnTPP·2Py (Table 2). Energy nonequivalence of pyridine molecules is probably due to the fact that the coordination of the second molecular ligand proceeds through the displacement of acido ligand in the outer coordination sphere of the complex [39]:

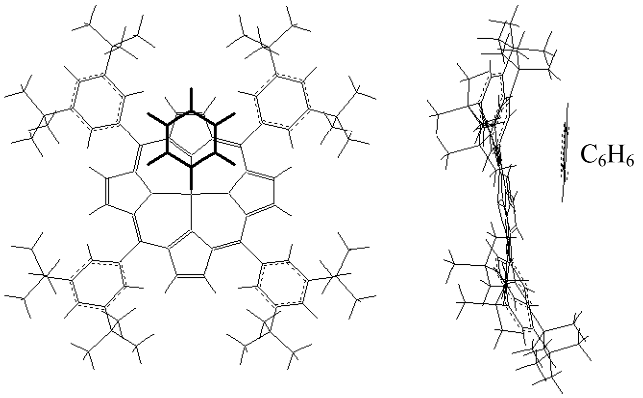


Fig. 2. Structure of the complex of MT(3,5-di-*t*-BuC$_6$H$_3$)P with benzene by the results of simulation in the framework of the MOPS algorithm [66].

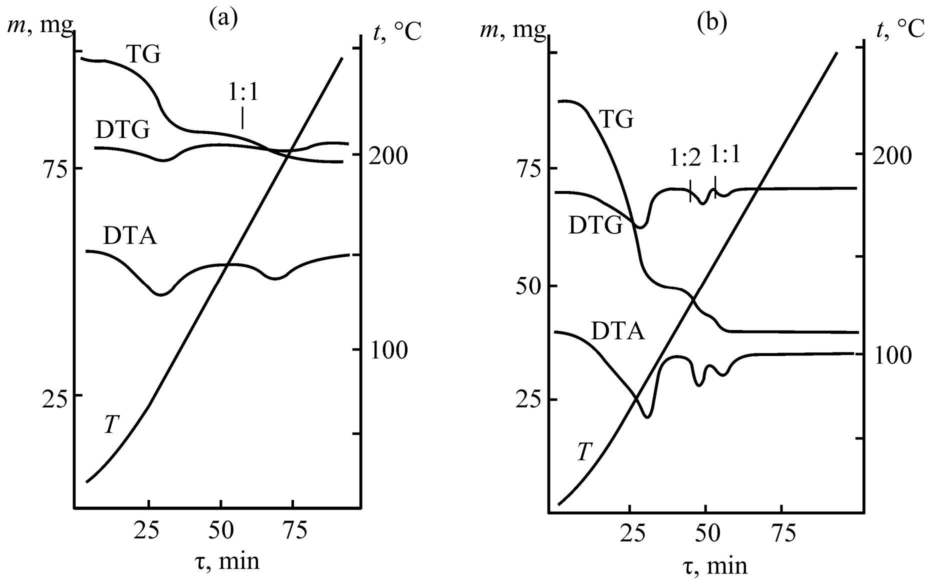
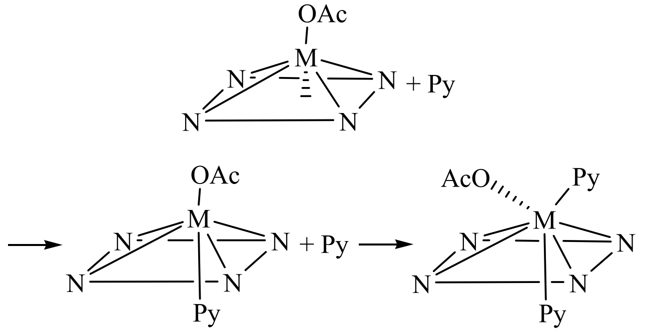


Fig. 3. Derivatogram of the crystal solvates (a) ZnT(3,5-di-*t*-BuC_6H_3)P with Py and (b) (AcO)MnT(3,5-di-*t*-BuC_6H_3)P with Py.



In the cases of the Mn(III), Cd(II), and Zn(II) complexes the introduction of *tert*-butyl substituents does not affect the composition of the formed crystal solvate with pyridine, but alters its thermal and energy stability. On the other hand, unlike NiTPP and CuTPP, NiT(3,5-di-*t*-BuC_6H_3)P and CuT(3,5-di-*t*-BuC_6H_3)P can form relatively stable 1:1 crystal solvates with pyridine. Apparently, the main causes of coordinative unsaturation of the Ni(II) and Cu(II) ions in the MT(3,5-di-*t*-BuC_6H_3)P are the electronic and steric effects of the alkyl substitution: a significant total $+I$ inductive effect of eight alkyl substituents weakens the reverse π-dative interaction of the metal with the macrocycle, increases the distortion of the planar structure of the latter and weakens the metal–ligand σ-interaction. Both factors contribute to the coordination unsaturation of the complex-forming cation.

These results obtained indicate that the probability of the formation of stable crystal solvates is the highest in the case of metalloporphyrins. Therefore, often the products of synthesis, chromatography, and recrystallization of metalloporphyrin carried out using benzene and its derivatives (toluene, xylenes, etc.) are the stable crystal solvates containing up to 7.10 wt % of the solvent. Moreover, the thermal destruction of many stable solvates is possible only at high (>100ºC) temperature. Even evacuation of the samples at lower temperatures to a constant weight often does not lead to the removal of the solvent. In such cases, to determine the composition of the crystalline sample and to select optimal conditions for the destruction of crystal solvates in order to obtain highly pure samples, the use of the TGA is the most effective and affordable.

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