

Thermophysical and structural properties of crystalline solvates of tetraphenylporphyrin and their zinc, copper and cadmium metallo-complexes

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Abstract

The results of a thermochemical and structural investigation of the process of desolvation of crystalline solvates of tetraphenylporphyrin H₂TPP with *o*-, *m*-xylene; zinc(II) tetraphenylporphyrin ZnTPP with benzene, toluene, *o*-, *m*-, *p*-xylene; cadmium(II) tetraphenylporphyrin CdTPP and copper(II) tetraphenylporphyrin CuTPP with *o*-, *m*-xylene are reported. Thermogravimetry and differential scanning calorimetry were used to determine the stoichiometry of crystalline solvates, the energy of activation and the heat effect of the desolvation process. The lattice parameters of the unsolvated crystalline CdTPP, ZnTPP and crystalline solvates of ZnTPP with *p*-xylene and CuTPP with *m*-xylene were determined using the X-ray powder diffraction method and the algorithm of Ito. The stoichiometry 1:1 for crystalline solvates [ZnTPP+(*p*-xylene)₁] and [CuTPP+(*m*-xylene)₁] was observed. The values of free volume per solvent molecules V^{free} defined as the difference between volume of unit cell of crystalline solvate and the sum of the volume of a unit cell of unsolvated phase of an investigated compound and Van der Waals volume of solvent molecules were calculated. The packing coefficients K_{chan} of the solvent molecules located in channels of the porphyrin matrix were also calculated. For ZnTPP crystalline solvates, we found the correlations between heat of desolvation and free volume per guest molecules of unit cell, as well as between the coefficient of channel packing and the temperature for which the half-lifetime of desolvation phase is equal to 60 min. A linear kinetic compensation effect for the crystalline solvates studied was found. © 1998 Elsevier Science B.V.

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1. Introduction

Porphyrins are cyclic aromatic polyamines based on a macrocycle skeleton containing 16 atoms. The interest in this type of compound arises from their unique

molecular structure. Investigations of structural properties of porphyrin sponges have advanced appreciably in recent years [1–4], as a result of advanced developed techniques available of growing organic crystals with programmable lattice architecture. The crystalline solvates contain three-dimensional channels occupied by solvent molecules (Fig. 1). Sizes of

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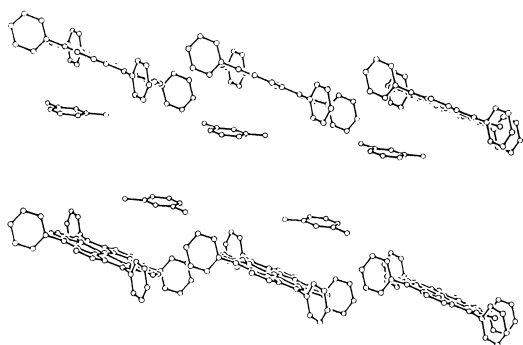


Fig. 1. A section parallel of the b and c axes for porphyrin sponges [1–4].

the channels may vary depending on the parameters of the crystal growing process and the geometry of guest molecules (the topological structure of porphyrin matrix does not change). Observation of the desolvation process suggests the possibility of removing a definite number of solvent molecules from the channels and therefore to control stoichiometry and the packing density of the channels as well as orientation of the guest molecules in the channels. The objective of this work is to find correlations between energetic and structural properties which characterize the evolution of selected crystalline phases. Presented further are the results of systematic thermophysical and structural investigations undertaken on the crystalline solvates based on tetraphenylporphyrin and its zinc(II), cadmium(II), and copper(II) metallo-complexes. The work is a continuation of our previous study [9] enlarging our knowledge by investigations of new groups of crystalline solvates.

2. Materials and methods

The free-base tetraphenylporphyrin H_2TPP and four-coordinate metallo-complexes tetraphenylporphyrin MTPP (where $M = Cu, Zn$ and Cd) were synthesized according to known methods [5,6]. All the compounds were thoroughly purified by repeated preparative chromatography (using a mixture of chloroform–benzene) and repeated recrystallization procedures. The final stages of purification were effected by carefully controlled sublimation techniques using a flow of inert gas (N_2) [7]. The absorption

spectra of these substances were found to conform to the literature data.

Benzene, toluene, *o*-, *m*-, *p*-xylene (Fluka) were dried by boiling with anhydrous $CaCl_2$ for 3 h. These solvents were twice distilled and stored in a protected (moisture-free) container.

All crystalline solvates were grown by slow evaporation of saturated solutions of the compounds followed by drying at room temperature. We did not succeed in preparing the crystalline solvates of H_2TPP from benzene, toluene and *p*-xylene solutions. Nevertheless, the X-ray data for $[H_2TPP + (p\text{-xylene})_1]$ are reported in the literature [1]. We believe that this phase is stable in saturated solution but in an air atmosphere at 298 K it quickly decomposes to the unsolvated state. Crystalline solvates $CdTPP$ obtained from solution were very unstable and therefore the TG measurements were performed immediately after the preparation.

X-Ray measurements were made using the Rigaku–Denki powder diffractometer, CuK_α radiation ($\lambda = 1.5418$), and Bragg–Brentano geometry. The powder diffraction pattern was scanned in steps of 0.05° (2θ) up to 50° and a fixed counting time (10 s) was employed. The calculation of the unit cell parameters and the identification of reflection planes were performed using the Ito algorithm [8].

The following parameters were calculated: the change of the unit cell volume of the crystalline solvate during process of desolvation ΔV ; the free volume per guest molecules V^{free} ; coefficients of crystalline solvate packing K_{cryst} ; and coefficients of packing of guest molecules in channels of porphyrin matrix K_{chan} .

The free volume per solvent molecules V^{free} defined as a difference between the volume of the unit cell of the crystalline solvate $V(Z[MTPP + (\text{solvent})_n])$ and the sum of the volume of unit cell of the unsolvated phase $V(Z[MTPP])$ of the compound and the Van der Waals volume of the solvent V_{solvent} located in the channels of porphyrin matrix were calculated according to the relations (1)–(2):

$$[MTPP + (\text{solvent})_n] \rightarrow [MTPP] + n \text{ solvent} \quad (1)$$

$$\begin{aligned} \Delta V &= V(Z[MTPP + (\text{solvent})_n]) - V(Z[MTPP]) \\ V^{free} &= \Delta V - ZnV_{\text{solvent}} \end{aligned} \quad (2)$$

where Z is the number of structure units of crystalline solvate in a unit cell; n is the number of molecules of a solvent.

The packing coefficient of crystalline solvate was calculated according to the relation:

$$K_{\text{cryst}} = (Z(nV_{\text{solvent}} + V_{\text{host}})) / V(Z[\text{MTPP} + (\text{solvent})_n]) \quad (3)$$

where V_{host} is the Van der Waals volume of porphyrin molecule.

The packing coefficient of a channel was calculated according to the relation:

$$K_{\text{chan}} = (ZnV_{\text{solvent}}) / \Delta V \quad (4)$$

The thermal properties of crystalline compounds were investigated in the range 298–623 K using a Du Pont Thermal Analysis System 2100, equipped with DSC 910 and TG 951 cells. The DSC device was calibrated using an indium sample and the TG cell was calibrated using of calcium oxalate monohydrate as described previously [9]. The relative error in thermal measurements was 1%. The DSC runs were performed at a scan rate of 10 K min⁻¹ in an atmosphere of flowing dry argon (100 ml min⁻¹) using open standard aluminium sample pans. On the basis of the TG curves obtained for various heating rates (0.5, 1, 2, 5, 10 and 20 K min⁻¹), the activation energy of the thermal processes E_a , the frequency or pre-exponential factor A , and the temperature, for which half-lifetime $t_{1/2}$, of desolvation phase is equal to 60 min, were calculated according to the model described in [10,11]:

$$d\alpha/dt = f(\alpha)[A \exp(-E_a/RT)] \quad (5)$$

where α is the fractional extent of reaction.

Assume, that $A, f(\alpha)$ and E are independent of T and that A and E are independent of α .

The TG Decomposition Kinetics Data Analysis Program, Version 4.0 Du Pont Analyst 2000/2100, was applied for these calculations.

In this work we do not attempt to describe the desolvation kinetic of the crystalline solvates using more complicated models. These problems will be an object of our subsequent investigations.

3. Results and discussion

The results of thermogravimetric and DSC investigations are given in Tables 1–3. The enthalpy effects

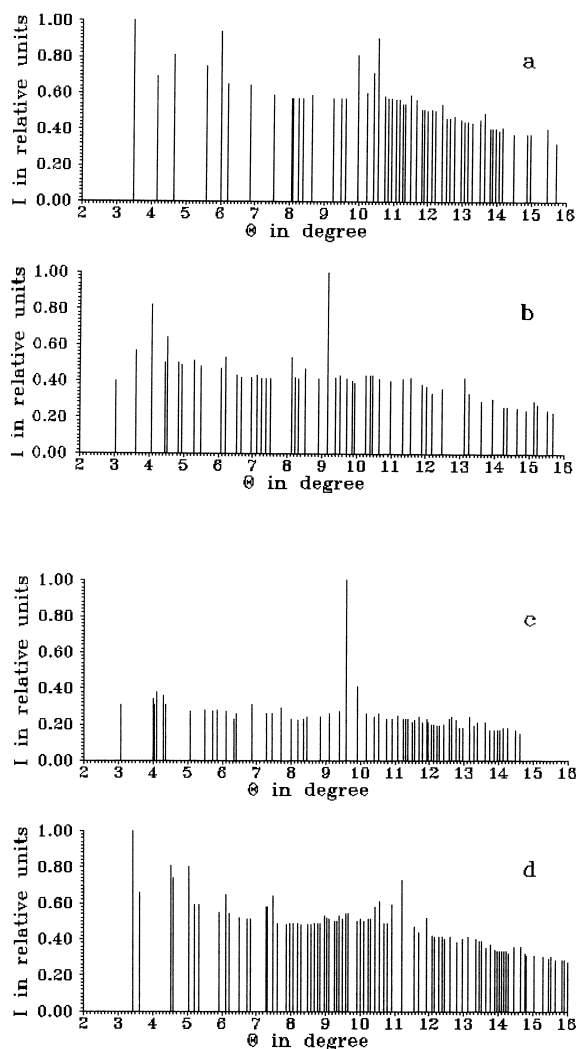


Fig. 2. The powder X-ray diffraction diagrams obtained for [ZnTPP] (a); [ZnTPP+(*p*-xylene)₁] (b); [CuTPP+(*m*-xylene)₁] (c) [CdTPP] (d).

of the desolvation process noted on the DSC curves are endothermic.

The X-ray data for unsolvated phases of [ZnTPP], [CdTPP] and for crystalline solvates [ZnTPP+(*p*-xylene)₁], [CuTPP+(*m*-xylene)₁] were measured by powder diffraction. Fig. 2 shows the X-ray diagrams obtained for the compounds investigated. The results of identification of the reflection planes of the first 20 peaks are given in Tables 4. Table 5 reviews the unit cells parameters of the crystalline phases. The X-ray

Table 1

The results of the thermogravimetric experiments for the reaction of desolvation at different heating rates, (β in K min⁻¹). The temperatures of start, T_s in K, and finish, T_f in K; the stoichiometry of crystalline solvate (host:guest), S

β	ZnTPP									
	Benzene		Toluene		<i>m</i> -xylene		<i>o</i> -xylene		<i>p</i> -xylene	
	T_s	T_f	T_s	T_f	T_s	T_f	T_s	T_f	T_s	T_f
0.5	—	—	305.3	332.6	317.6	350.1	318.6	363.2	—	—
1	310.3	357.8	307.0	345.5	320.3	355.8	320.1	378.2	345.9	408.8
2	314.0	368.7	309.7	351.2	324.8	359.0	325.8	396.8	351.1	415.1
5	314.8	373.8	311.2	360.7	328.9	368.1	327.4	408.3	367.7	429.6
10	324.7	383.8	313.2	372.7	331.3	377.5	331.8	414.4	370.9	441.9
20	324.7	393.4	314.2	385.4	336.9	395.1	333.2	431.7	382.2	458.1
S	1:2		1:2		1:2		1:2		1:1	
β	H ₂ TPP				CdTPP					
	<i>m</i> -xylene		<i>o</i> -xylene		<i>m</i> -xylene		<i>o</i> -xylene			
	T_s	T_f	T_s	T_f	T_s	T_f	T_s	T_f		
0.5	—	—	297.4	325.5	296.2	311.6	—	—		
1	317.9	366.4	297.9	358.8	296.2	315.2	296.2	327.6		
2	325.7	370.3	298.5	365.9	296.2	320.7	296.2	336.9		
5	329.7	374.3	299.0	375.0	296.2	333.0	296.4	342.7		
10	337.3	380.9	299.2	387.0	297.2	343.3	296.5	366.2		
20	336.4	330.0	299.7	397.4	297.5	368.6	297.2	373.7		
S	1:2		1:2		1:2			1:2		

Table 2

The results of the thermogravimetric experiments for the reaction of desolvation at different heating rates, (β in K min⁻¹). The temperatures of start, T_s in K, and finish, T_f in K; Δ_m in %; AML – the average mass losses (%); the stoichiometry of reaction, SR; the stoichiometry of crystalline solvate (host:guest), S

β	CuTPP+(<i>m</i> -xylene)				CuTPP+(<i>o</i> -xylene)			
	First stage		Second stage		First stage		Second stage	
	T_s/T_f	Δ_m	T_s/T_f	Δ_m	T_s/T_f	Δ_m	T_s/T_f	Δ_m
1	322.9/355.7	8.1	355.4/452.4	4.7	—	—	—	—
2	327.9/361.9	8.1	363.3/452.0	4.8	303.2/438.8	18.1	438.8/503.2	2.9
5	329.8/365.1	7.9	364.7/453.2	4.9	303.2/446.2	18.2	446.2/522.2	3.1
10	330.8/369.7	7.9	370.2/514.2	5.1	303.2/473.2	18.3	473.2/540.2	3.0
20	336.0/379.9	8.3	378.9/559.2	5.1	—	—	—	—
AML		8.1		4.9		18.2		3.0
SR	(5:5)→(5:2)		(5:2)→(5:0)		(20:20)→(20:3)		(20:3)→(20:0)	
S	1:1				1:2			

literature data for the crystalline phases studied by us [1–4,12,13,15,18] (Table 6) and the data obtained here for the unknown phases were used for calculations of the ΔV , V^{free} , K_{cryst} and K_{chan} values (Table 7).

The thermogravimetric and DSC data indicate that crystalline solvates ZnTPP with benzene, toluene, *o*-,

m-xylene have stoichiometry (1:2), similar to those observed in the case of crystalline solvates H₂TPP, CdTPP with *o*-, *m*-xylene. This is in good agreement with the data obtained by X-ray investigations [1–4]. The process of desolvation of these compounds occurs in one stage with loss of all solvent molecules from the lattice:

Table 3

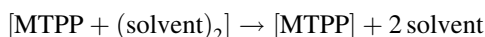
The activation energy, E_a in kJ mol^{-1} ; heat effect, Q in kJ mol^{-1} ; pre-exponential factor, $A=10^\nu$ in min^{-1} , of desolvation process; the temperature, $t_{1/2}$ in K, for which half-lifetime of desolvation phase is equal 60 min

Crystalline solvates	E_a		Q^a		ν		$t_{1/2}$		M^b
	First	Second	First	Second	First	Second	First	Second	
ZnTPP+(benzene) ₂	120±1	—	77.2	—	17.3	—	326	—	834.31
ZnTPP+(toluene) ₂	80±2	—	127	—	12.0	—	308	—	862.37
ZnTPP+(<i>m</i> -xylene) ₂	117±1	—	145	—	17.0	—	324	—	890.43
ZnTPP+(<i>o</i> -xylene) ₂	104±1	—	120	—	14.4	—	333	—	890.43
ZnTPP+(<i>p</i> -xylene) ₁	86.0±0.5	—	72.1	—	10.5	—	326	—	784.27
H ₂ TPP+(<i>m</i> -xylene) ₂	108±1	—	113.4	—	15.5	—	325	—	827.02
H ₂ TPP+(<i>o</i> -xylene) ₂	59±1	—	55.5	—	8.7	—	289	—	827.02
CdTPP+(<i>m</i> -xylene) ₂	91±3	—	71.0	—	15.0	—	285	—	937.46
CdTPP+(<i>o</i> -xylene) ₂	65±3	—	61.6	—	10.0	—	284	—	937.46
CuTPP+(benzene) ₁ ^c	79±1	102±1	7.6	2.9	10.0	10.2	337	436	754.39
CuTPP+(<i>m</i> -xylene) ₁	182±2	68.0±0.5	33.6	6.4	27.0	7.8	331	364	782.45
CuTPP+(<i>o</i> -xylene) ₂	49±1	100±1	5.4	7.2	6.0	10.1	323	435	782.45

^a The relative error in thermal measurements was 1%.

^b Molecular mass of crystalline solvate.

^c Ref. [9].



From Table 1 it follows, that ZnTPP forms numerous groups of crystalline solvates, having different solvent molecules and the same stoichiometry: $[\text{ZnTPP} + (\text{solvent})_2]$ where the solvent is benzene, toluene, *o*-, *m*-xylene. Therefore we have attempted to analyse the influence of the nature of guest molecules on the thermal behaviour of the desolvation process for this group of the compounds.

The value of Q is a summarized characteristic of all heat effects occurring during desolvation. A volume of unit cell is very sensitive to all kinds of interactions of molecules in a crystal. We have attempted to find a correlation between Q and V^{free} for $[\text{ZnTPP} + (\text{solvent})_2]$ (Fig. 3). From Fig. 3, we conclude that an increase of V^{free} leads to an increase of Q . Simultaneously it is known that the value V^{free} for crystalline solvates of analogous architecture is related, mainly with topology of the guest molecule and the geometrical conjugation of guest–guest and guest–host in a channel of porphyrin matrix [16]. Presumably for crystalline solvates $[\text{ZnTPP} + (\text{solvent})_2]$, the heat effect of desolvation is connected with the act of free volume activation in the crystalline lattice.

The dependence of the temperature $t_{1/2}$ for which the half-lifetime for desolvation of the phase is equal

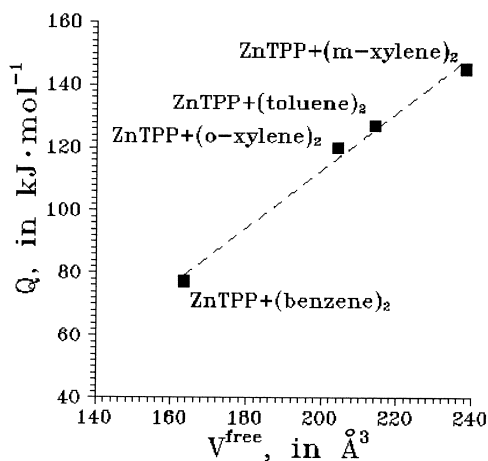


Fig. 3. The dependence of a heat effect of desolvation process, Q , versus a free volume per solvent molecules in a unit cell, V^{free} , for the crystalline solvates by based ZnTPP.

to 60 min, versus the packing coefficient of channel K_{chan} is presented in Fig. 4. The thermal stability of the studied $[\text{ZnTPP} + (\text{solvent})_2]$ crystalline system increases with increase of the K_{chan} . For example, the crystal ZnTPP with *o*-xylene is more thermally stable ($K_{\text{chan}}=0.698$ and $t_{1/2}=333$ K), whereas ZnTPP with toluene is one of less stable ($K_{\text{chan}}=0.655$ and $t_{1/2}=308$ K).

Table 4

The experimental, $(d/n)_e$ in Å, and theoretical, $(d/n)_t$ in Å, values of distance between planes of reflection; the intensity, I in relative units, and the indexes, (hkl), for first 20 reflections

No.	$(d/n)_e$	$(d/n)_t$	I	(hkl)	$(d/n)_e$	$(d/n)_t$	I	(hkl)
CuTPP+(<i>m</i> -Xylene) ₁					CdTPP			
1	14.49±0.15	14.49	0.31	(100)	12.94±0.15	12.94	1.00	(100)
2	11.06±0.15	11.06	0.34	(010)	12.20±0.15	12.20	0.66	(010)
3	10.92±0.15	10.93	0.31	(1 $\bar{1}$ 0)	9.77±0.08	9.77	0.81	(001)
4	10.79±0.15	10.79	0.38	(001)	9.61±0.08	9.59	0.74	(1 $\bar{1}$ 0)
5	10.31±0.15	10.31	0.36	(01 $\bar{1}$)	8.79±0.08	8.80	0.80	(01 $\bar{1}$)
6	10.11±0.15	10.07	0.31	(10 $\bar{1}$)	8.50±0.08	8.52	0.59	(10 $\bar{1}$)
7	8.70±0.08	8.74	0.27	(1 $\bar{1}$ 1)	8.31±0.08	8.30	0.59	(110)
8	8.03±0.08	8.10	0.28	(11 $\bar{1}$)	7.48±0.08	7.45	0.55	(11 $\bar{1}$)
9	7.73±0.08	7.71	0.27	(101)	7.22±0.08	7.23	0.65	(101)
10	7.56±0.08	7.56	0.28	(110)	7.11±0.08	7.12	0.54	(1 $\bar{1}$ 1)
11	7.22±0.08	7.25	0.27	(200)	6.81±0.08	6.82	0.52	(011)
12	6.99±0.08	6.96	0.23	(20 $\bar{1}$)	6.57±0.08	6.59	0.51	(1 $\bar{1}$ 1)
13	6.89±0.08	6.93	0.26	(1 $\bar{1}$ 1)	6.49±0.08	6.47	0.51	(200)
14	6.44±0.08	6.44	0.31	(011)	6.095±0.02	6.095	0.58	(020)
15	6.09±0.08	6.08	0.26	(2 $\bar{1}$ 1)	6.09±0.02	6.09	0.58	(2 $\bar{1}$ 0)
16	5.94±0.08	5.94	0.26	(01 $\bar{2}$)(1 $\bar{2}$ 0)	5.93±0.02	5.89	0.64	(021)(20 $\bar{1}$)
17	5.75±0.05	5.76	0.29	(21 $\bar{1}$)(11 $\bar{2}$)	5.82±0.02	5.84	0.49	(1 $\bar{2}$ 0)
18	5.53±0.02	5.53	0.23	(020)(10 $\bar{2}$)	5.57±0.02	5.59	0.49	(111)
19	5.41±0.02	5.40	0.22	(020)(2 $\bar{2}$ 1)	5.49±0.02	5.44	0.49	(1 $\bar{2}$ 1)
20	5.33±0.02	5.35	0.23	(1 $\bar{1}$ 2)	5.40±0.02	5.40	0.49	(210)
Zn(TPP)+ <i>p</i> -Xylene) ₁					ZnTPP			
1	14.59±0.15	14.59	0.40	(100)	12.73±0.15	12.73	1.00	(100)(010)
2	12.27±0.15	12.27	0.57	(010)	10.62±0.15	10.68	0.69	(1 $\bar{1}$ 0)
3	10.90±0.15	10.90	0.82	(001)	9.50±0.08	9.50	0.81	(001)
4	9.94±0.08	9.91	0.50	(1 $\bar{1}$ 0)	7.90±0.08	7.91	0.75	(110)(01 $\bar{1}$)(10 $\bar{1}$)
5	9.79±0.08	9.79	0.64	(01 $\bar{1}$)	7.35±0.08	7.35	0.94	(011)(101)
6	9.10±0.08	9.14	0.50	(10 $\bar{1}$)	7.13±0.08	7.10	0.65	(1 $\bar{1}$ 1)(1 $\bar{1}$ 1)
7	8.96±0.08	8.94	0.49	(110)	6.44±0.08	6.50	0.64	(1 $\bar{2}$ 0)(2 $\bar{1}$ 0)
8	8.34±0.08	8.37	0.51	(101)	5.86±0.05	5.82	0.59	(111)
9	8.05±0.08	8.12	0.48	(11 $\bar{1}$)	5.50±0.05	5.48	0.57	(021)(20 $\bar{1}$)
10	7.28±0.08	7.30	0.47	(200)	5.47±0.05	5.46	0.57	(1 $\bar{2}$ 1)(2 $\bar{1}$ 1)
11	7.12±0.08	7.13	0.53	(011)	5.37±0.05	5.34	0.57	(2 $\bar{2}$ 0)
12	6.76±0.08	6.73	0.43	(1 $\bar{1}$ 1)	5.21±0.05	5.26	0.57	(2 $\bar{1}$ 1)(1 $\bar{2}$ 1)
13	6.64±0.08	6.58	0.42	(2 $\bar{1}$ 0)	5.12±0.02	5.11	0.59	(021)(210)(201)
14	6.37±0.08	6.34	0.42	(20 $\bar{1}$)	4.77±0.02	4.75	0.57	(002)
15	6.22±0.08	6.23	0.43	(02 $\bar{1}$)	4.68±0.02	4.69	0.57	(12 $\bar{1}$)(21 $\bar{1}$)
16	6.11±0.02	6.12	0.41	(020)(111)	4.61±0.02	4.66	0.57	(221)(2 $\bar{2}$ 1)
17	6.00±0.02	6.00	0.41	(210)	4.45±0.02	4.43	0.81	(130)(310)
18	5.90±0.02	5.88	0.41	(1 $\bar{2}$ 0)	4.34±0.02	4.34	0.60	(012)(102)(1 $\bar{1}$ 2)
19	5.45±0.02	5.45	0.53	(002)(120)(2 $\bar{1}$ 1)	4.26±0.02	4.25	0.71	(11 $\bar{2}$)
20	5.39±0.02	5.37	0.42	(11 $\bar{2}$)	4.22±0.02	4.24	0.90	(030)(300)

For the TG and DSC investigations from a *p*-xylene solution, we were able to obtain only the crystalline solvate [ZnTPP+(*p*-xylene)₁] (Table 1). Nevertheless, in the literature [2] there are reported results for crystalline solvates of ZnTPP with *p*-xylene of

different stoichiometry: [ZnTPP+(*p*-xylene)₂] and [ZnTPP₂+(*p*-xylene)₁]. The [ZnTPP+(*p*-xylene)₂] is thermodynamically unstable and can be obtained as a kinetic product by seeding a saturated solution with crystals of [ZnTPP+(*o*-xylene)₂]. The [ZnTPP₂+

Table 5

Lattice parameters ^a for investigated compounds calculated following Ito method

Compounds	Å			deg			Vol Å ³	Z
	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ		
ZnTPP	13.32	13.32	9.54	93	93	107	1615	2
ZnTPP+(<i>p</i> -xylene) ₁	12.94	11.48	14.70	94	95	108	2067	2
CuTPP ^b	13.97	12.39	11.56	110	102	108	1673	2
CuTPP+(benzene) ₁ ^b	18.03	16.94	15.10	90	90	115	4185	4
CuTPP+(<i>m</i> -xylene) ₁	15.71	12.84	12.12	112	98	107	2087	2
CdTPP	13.20	12.68	10.20	104	98	96	1626	2

^a Relative accuracy: *a*, *b*, *c* – 1%; α , β , γ – 2%.^b Ref. [9].

Table 6

Lattice parameters for investigated compounds

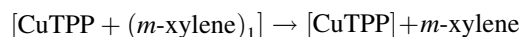
Compounds	Å			deg			Vol ^a Å ³	Z	Space group	Ref.
	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ				
ZnTPP	14.8	17.2	14.6	90	90	90	3716.6	4	P2 ₁ 2 ₁ 2 ₁	[12]
ZnTPP	10.382	12.421	6.443	98.30	101.15	96.47	798.1	1	P $\bar{1}$	[13]
ZnTPP+(benzene) ₂	18.386	15.819	10.867	90	137.87	90	2120	2	P2 ₁ /n	[4]
ZnTPP+(toluene) ₂	11.349	11.404	10.502	110.48	103.87	107.65	2237	2	P $\bar{1}$	[18]
ZnTPP+(toluene) ₂	18.212	15.229	10.430	90	134.23	90	(2073)	2	P2 ₁ /n	[4]
ZnTPP+(<i>m</i> -xylene) ₂	13.465	21.709	11.174	64.80	51.98	72.99	2326	2		[1]
ZnTPP+(<i>o</i> -xylene) ₂	13.677	21.975	10.975	66.94	49.16	72.97	2292	2		[1]
ZnTPP+(<i>p</i> -xylene) ₂	13.566	22.435	11.296	65.06	46.72	73.40	2269	2		[2]
H ₂ TPP	6.44	10.42	12.41	96.06	99.14	101.12	801.9	1	P $\bar{1}$	[17]
H ₂ TPP+(<i>m</i> -xylene) ₂	13.632	19.389	12.020	54.87	63.11	70.97	2308	2		[1]
H ₂ TPP+(<i>p</i> -xylene) ₁	13.667	17.692	14.470	60.85	43.34	80.94	1981	2		[1]
CdTPP+(<i>m</i> -xylene) ₂	13.563	21.970	10.995	65.76	51.55	72.55	2335	2		[2]
CdTPP+(<i>o</i> -xylene) ₂	13.807	22.109	11.085	66.97	48.52	73.03	2330	2		[2]
CuTPP+(<i>m</i> -xylene) ₂	13.528	19.098	11.984	53.71	63.87	70.88	(2231)	2		[2]

^a A volume in parentheses indicates a low-temperature structure determination.

(*p*-xylene)₁] is directly crystallized from a saturated solution. One molecule of *p*-xylene located in the channel of crystalline lattice [ZnTPP+(*p*-xylene)₁] has V^{free} approximately 1.5 times greater than in crystalline solvate with stoichiometry (1:2). Probably, the *p*-xylene molecule in relation to its largest linear dimension is located in the channel lengthwise. Analogous behaviour was observed in the case of [H₂TPP+(*p*-xylene)₁] described in [1].

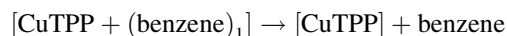
The crystalline solvates based on CuTPP were prepared only for *o*-, *m*-xylene. Their stoichiometry was (1:2) and (1:1) respectively. The crystalline [CuTPP+(benzene)₁] has been studied by us earlier [9]. The kinetics of desolvation is very similar for this group of crystalline solvates: (a) the process occurs in two independent stages (Table 2); (b) these stages are

separated one from another on the temperature scale. It allows characterization of each stage (Table 3). The process of desolvation can be presented as follows:



First stage: (5:5)→(5:2)

Second stage: (5:2)→(5:0)



First stage: (5:5)→(5:3)

Second stage: (5:3)→(5:0)

It can be seen, that for crystalline solvate with *m*-xylene, the major part of the solvent molecules leave the crystal lattice during the first stage of desolvation, whereas for [CuTPP+(benzene)₁], this occurs during the second stage.

Table 7

Unit cell volume of starting, V_1 , and final, V_2 , crystal structure and the volume loss during desolvation, ΔV ; free volume per guest molecules, V^{free} ; packing coefficient of guest molecules in channels of porphyrin matrix, K_{chan} ; packing coefficient of molecules in unit cell of crystalline solvate, K_{cryst}

Reactions of desolvation	$\text{\AA}^3$				K_{chan}	K_{cryst}
	V_1	V_2	ΔV	V^{free}		
$[\text{ZnTPP} + (\text{benzene})_2] \rightarrow [\text{ZnTPP}]$	2120 ^a	1615 ^b	505	163	0.676	0.729
$[\text{ZnTPP} + (\text{toluene})_2] \rightarrow [\text{ZnTPP}]$	2237 ^c	1615 ^b	622	215	0.655	0.720
$[\text{ZnTPP} + (m\text{-xylene})_2] \rightarrow [\text{ZnTPP}]$	2326 ^d	1615 ^b	711	238	0.665	0.721
$[\text{ZnTPP} + (o\text{-xylene})_2] \rightarrow [\text{ZnTPP}]$	2292 ^a	1615 ^b	677	204	0.698	0.732
$[\text{ZnTPP} + (p\text{-xylene})_1] \rightarrow [\text{ZnTPP}]$	2067 ^b	1615 ^b	452	216	0.523	0.697
$[\text{H}_2\text{TPP} + (m\text{-xylene})_2] \rightarrow [\text{H}_2\text{TPP}]$	2308 ^d	1604 ^g	704	231	0.672	0.707
$[\text{CdTPP} + (m\text{-xylene})_2] \rightarrow [\text{CdTPP}]$	2335 ^e	1626 ^b	709	236	0.667	0.719
$[\text{CdTPP} + (o\text{-xylene})_2] \rightarrow [\text{CdTPP}]$	2330 ^e	1626 ^b	704	231	0.672	0.721
$[\text{CuTPP} + (\text{benzene})_1] \rightarrow [\text{CuTPP}]$	2093 ^f	1673 ^f	420	249	0.407	0.656
$[\text{CuTPP} + (m\text{-xylene})_1] \rightarrow [\text{CuTPP}]$	2087 ^b	1673 ^f	414	178	0.571	0.689

^a Ref. [4].

^b This work.

^c Ref. [18].

^d Ref. [1].

^e Ref. [2].

^f Ref. [9].

^g Ref. [17]

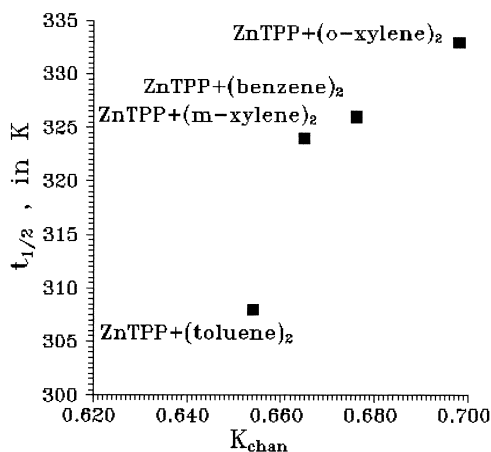
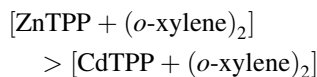
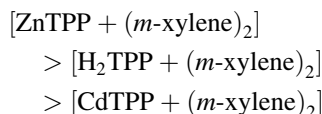


Fig. 4. The dependence of a temperature for which half-lifetime of desolvation phase equals to 60 min, $t_{1/2}$, versus a coefficient of packing guest molecules in channels of porphyrin matrix, K_{chan} , for the crystalline solvates by based ZnTPP.

An influence of the nature of porphyrin molecule (host) of crystalline solvate on energetics of the desolvation process was analysed as an example of crystal matrixes, which have the same solvate (guest) molecules but different host molecules: $[\text{MTPP} + (m\text{-xylene})_2]$ and $[\text{MTPP} + (o\text{-xylene})_2]$, where $M = \text{H}_2$; Zn; Cd; Cu.

We observed that for the crystalline solvates with similar values of the coefficient K_{chan} , there is a certain regularity in absolute values of heat of desolvation for different compounds with *o*-, *m*-xylene:



The examination of the data in Table 3 indicates that the total heat effect of solvation Q is different for different host molecules. We assumed that Q depends on nonspecific guest–host interactions.

As a measure of these interactions, we have chosen values of partial molar volumes of the host $\bar{V}_2^0$ in benzene solutions. Then, the relation between Q and $\bar{V}_2^0$ was derived (Fig. 5). It was found, that interactions with the solvent molecules are stronger in the case of ZnTPP molecules than for H_2TPP , CdTPP and CuTPP. It is very likely due to the more favorable redistribution of electron density between metal atom and the porphyrin macrocycle.

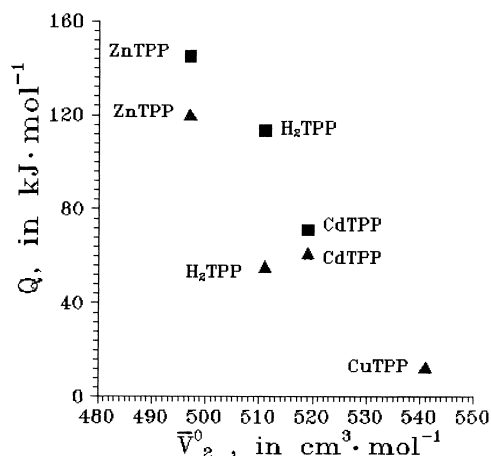


Fig. 5. The dependence of a heat effect of desolvation process, Q , versus a MTPP partial molar volume, $\bar{V}_2^0$, in benzene. ■ – [MTPP+(*m*-xylene)₂]; ▲ – [MTPP+(*o*-xylene)₂].

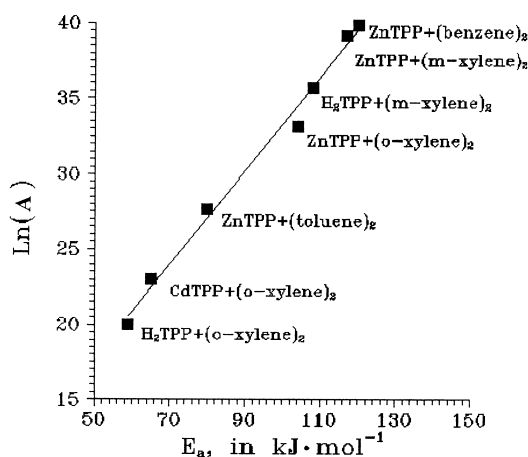


Fig. 6. The dependence of $\text{Ln}(A)$ versus an energy of activation, E_a , of a crystalline solvates [MTPP+(solvent)₂].

The dependences of $\text{Ln}(A)$ versus energy of activation of crystalline solvates: [MTPP+(solvent)₂], where $M=\text{H}_2$; Zn; Cd are presented in Fig. 6. As can be seen from these figures, the relation can be approximated as a straight line (linear kinetic compensation effect) [14]:

$$\text{Ln}(A) = (2.2 \pm 1.3) + (0.31 \pm 0.01)E_a \quad (6)$$

$$s = 0.814 \quad r = 0.995 \quad n = 7$$

The observed behaviour of the kinetical parameters suggests an identical mechanism of the desolvation

process of the investigated crystalline solvates with stoichiometry 1:2.

4. Conclusion

The presented experimental results lead to the conclusion that the thermal stability of crystalline solvates [ZnTPP+(solvent)_n] is connected with such structural parameter as the packing coefficient K_{chan} of the solvent molecules located in the channels of the porphyrin matrix. The heat effect Q of desolvation process of investigated compounds is sensitive to: (a) the value of free volume per solvent (guest) molecule V^{free} ; (b) the nature of the metal atom of MTPP (host); (c) the nature of the solvent (guest) molecule.

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