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Thermophysical and structural investigations of crystalline solvates based on tetraphenylporphyrin and its copper complex

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Abstract

The influence of temperature changes on the thermal and structural behaviour of crystalline solvates of tetraphenylporphyrin (H_2TPP) with 1,4-dioxane and of tetraphenylporphyrin copper complexes (CuTPP) with benzene were investigated using thermogravimetry, differential scanning calorimetry and X-ray powder diffraction. Simultaneous application of thermal and structural techniques made it possible to observe the complex evolution of the desolvation processes. These techniques enabled: (a) the separation of the two crystalline phases appearing during the process, (b) the detection of changes of the symmetry of the crystal lattice of CuTPP crystalline solvate from monoclinic and triclinic, (c) the determination of the heat and activation energy of desolvation process, and (d) the observation of reversible thermal effects for H_2TPP.

Keywords: Symmetry changes; Tetraphenylporphyrin; Tetraphenylporphyrin copper complexes; Thermal behaviour; X-ray.

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1. Introduction

Porphyrins are cyclic aromatic polyamines based on a macrocyclic skeleton containing 16 atoms. The interest in studying these compounds results from their unique molecular structure which determines important biological activity. For instance,

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porphyrins are involved in protein complexation reactions, and in many oxidation–reduction reactions associated with oxygen transfer in the living cell. Recently, application of tetraphenylporphyrin sponges as a size-selective membrane, as a programmable photoconductor, and as matrices in which controlled photosynthetic reactions may take place has been investigated [1–3]. Investigations of host–guest systems are based on the determination of their thermodynamic properties and of interatomic interactions in the crystalline state of the compounds studied. Therefore it seemed especially interesting to determine simultaneously both energetic and structural properties which could characterize the evolution of selected crystalline solvates.

Solvates based on tetraphenylporphyrin (H_2TPP) and its copper complex (CuTPP) with 1,4-dioxane and benzene, respectively, were chosen as objects of the present study (the structural formulae of these compounds are given in Fig. 1). H_2TPP and CuTPP were chosen for investigations because they serve as models for this class of compound, whereas benzene and 1,4-dioxane are typical solvents for obtaining monocrystals of these compounds. There is also plenty of experimental data relating to the structural properties of their monocrystals and crystalline solvates [1–4]. However the results of these structural investigations do not correlate with the energetic properties of these compounds. For this reason the simultaneous investigations of structural and thermal properties of the compounds discussed below were undertaken.

2. Experimental

2.1 Materials

The free base tetraphenylporphyrin and its four-coordinate copper complex were synthesized according to known methods [5, 6]. The compounds were thoroughly

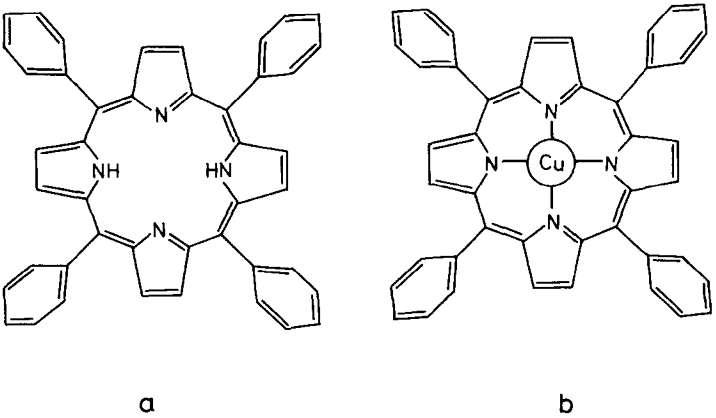


Fig. 1. The structural formulae of tetraphenylporphyrin H_2TPP (a), and tetraphenylporphyrin copper complex, CuTPP (b).

purified by repeated preparative chromatography with Al_2O_3 and chloroform–benzene as eluent. The compounds were then recrystallized from this solvent mixture by addition of excess CH_3OH. The final stages of purification were performed by carefully controlled sublimation using the flow of inert gas method [7]. The absorption spectra of the substances studied were found to conform with literature data. The 1,4-dioxane and benzene were purified and dried using standard methods [8]. Crystalline solvates H_2TPP + 1,4-dioxane and CuTPP + benzene were crystallized from saturated solutions by vaporization in an atmosphere of flowing dry N_2 at a temperature of 333 K. The polycrystals obtained were kept in an hermetically sealed vessel before the experiments.

2.2. DSC and TG analyses

The thermal properties of the crystalline compounds were investigated in the range of 298 to 823 K using a Du Pont TGA 951 thermogravimetric analyser and a DSC 910 differential scanning calorimeter. The DSC was calibrated using an indium sample obtained from the Polish Committee for Standardization, Measures and Quanlity Control (Warsaw, Poland). The value of the determined enthalpy of fusion corresponded to -28.5 J g^{-1} (recommended value -28.4 J g^{-1}). The relative error in thermal measurements was 1%. The determined temperature of melting was 429.3 ± 0.1K; the onset of the melting curve should appear at 429.6 K.

Calibration of the TGA cell was performed using a sample of calcium oxalate monohydrate in an atmosphere of flowing dry argon (100 mL min^{-1}) a heating rate of 5 K min^{-1}. The accuracy of the weight measurements was 1%. The inflection temperature of the first transition (dehydration) corresponded to 426.9 ± 1 K and the loss of bound water was equal to 12.5%. The Kinetics Data Analysis Program, Version 4.0 for Du Pont Thermal Analyst 2100 was applied for the calculation of the activation energies. They were calculated from the TG curves obtained at the 50% conversion level [9,10]. The determinations were performed at various heating rates ($\beta = 1, 2, 5, 10$ and 20 K min^{-1}).

2.3. X-ray analysis

X-ray measurements were made using the Rigaku-Denki powder diffractometer, CuK_α radiation, and Bragg–Brentano geometry. The measurements were made in an X-ray in situ environmental chamber in which the temperature was controlled with an accuracy of ± 1 K. We used an argon atmosphere and carried out the experiment within the temperature range 298 to 673 K. The calculation of the unit cell parameters and the identification of reflection planes were performed using the algorithm of Ito [11].

3. Results and discussion

The data from TG, DTG and DSC investigations of the crystalline solvates CuTPP + benzene are collected in Table 1 and graphically presented in Fig. 2a, b. The

Table 1
The mass losses, Δm in %, of the CuTPP + benzene and H_2TPP + benzene + 1,4-dioxane crystalline solvates from TG data recorded at different β in K min^{-1}

β	CuTPP + benzene Δm		H_2TPP + 1,4-dioxane Δm	
	First stage	Second stage	First stage	Second stage
1	2.0	5.8	3.3	2.5
2	2.0	5.9	3.5	2.3
5	2.1	5.6	3.0	2.3
10	2.2	5.6	3.2	2.1
20	2.1	5.8	3.1	2.0
Average	2.1	5.7	3.2	2.2

results of the thermogravimetric experiments indicate two distinct stages of mass loss. The first stage takes place in the temperature interval 320 to 420 K, the second is observed in the range 420 to 570 K. The position of peaks on DTG curves (midpoint of transformation) depends on the heating rate, β, applied in the experiment. As is shown in Fig. 2b, comparison of the DTG and DSC curves for $\beta = 10$ K min^{-1} suggests that both transformations observed on the DTG curves are endothermic processes. Mass losses and corresponding heat effects observed in the two stages appear in similar temperature ranges. The temperatures of peaks in DTG and DSC curves are also similar. The first transformation, characterized by mass loss $\Delta m_1 = 2.2\%$ and a peak on the DTG curve at $T_p = 385.1$ K is evidently related to a heat of $\Delta Q_1 = 7.6$ kJ mol^{-1} with a minimum on the DSC curve at $T_p^* = 385.4$ K. The second mass loss ($\Delta m_2 = 5.6\%$) takes place over a large temperature range (415 to 560 K) with a maximum on the DTG curve at $T_p = 510.5$ K. The shape of the corresponding part of DSC curve in this range indicates at first (420 to 490 K) a slow process of almost constant heat production. This is followed by a short lasting process characterized by a heat of $\Delta Q_2 = 2.9$ kJ mol^{-1} with a peak at $T_p^* = 503.8$ K.

On the basis of these results it was assumed that the observed thermal behaviour of the complexes characterizes the desolvation process which proceeds in two independent stages. In the first, as can be seen from the data in Table 1, there is a change of stoichiometry of the solvated complex from 4:4 to 4:3. The determination of the activation energy is interesting. First, in order to confirm the correctness of the assumption that the two stages are independent, for both stages the function $\log(\beta) = f(1/T)$ was plotted for different values for the fractional extent of reaction, α (Fig. 3). As can be seen from this figure, a good correlation is observed for $\alpha = 30\%$, 40%, 50% and 60%. The first desolvation stage activation energies are also consistent: $E_a^1(30\%) = 81.4$ kJ mol^{-1}, $E_a^1(40\%) = 79.6$ kJ mol^{-1}, $E_a^1(50\%) = 77.6$ kJ mol^{-1}, $E_a^1(60\%) = 75.3$ kJ mol^{-1}, $E_a^{-1} = 79 \pm 1$ kJ mol^{-1}.

In the second desolvation stage the solvent molecules leave the crystal lattice and the stoichiometry of the studied compounds changes from 4:3 to 4:0. The course of the TG

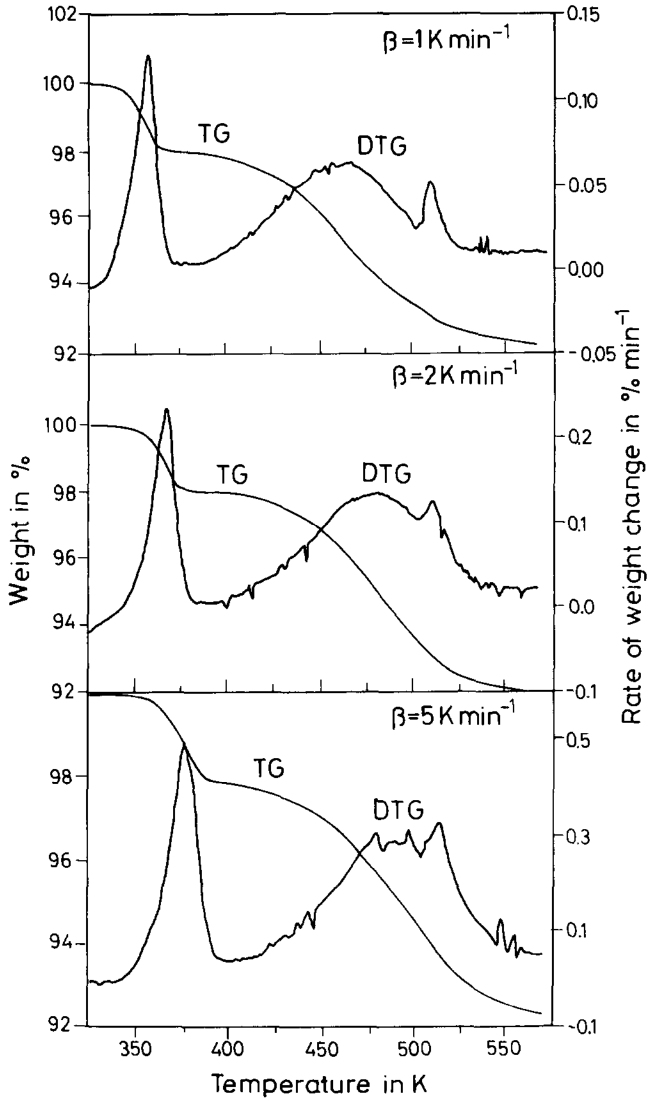


Fig. 2. Thermal behaviour of crystalline solvates CuTPP + benzene. (a) TG and DTG curves for heating rates 1,2 and 5 K min^{-1}; (b) TG, DTG and DSC curves for $\beta = 10$ K min^{-1}.

and DTG curves for heating rates smaller than $\beta = 10$ K min^{-1} reveals the greater complexity of this desolvation stage (Fig. 2a). This is especially pronounced in the higher temperature range. To calculate the value of the second desolvation stage activation energy, the data for $\alpha = 30\%$, 40% and 50% was taken into account. The data for the low values of α were not examined, to avoid errors of calculation linked to the overlap of the ending of the first stage with the beginning of the second stage curve.

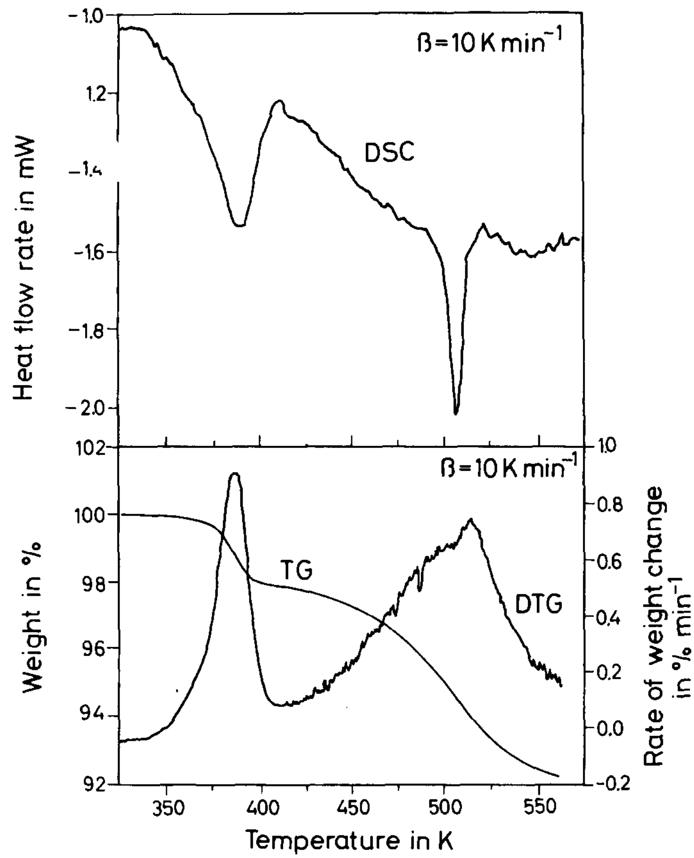


Fig. 2b

Interpretation of these data is also complicated because of the complex character of nucleation process. For α values of 30%, 40% and 50% the E_a^2 values are equal to 103.3 kJ mol^{-1}, 100.3 kJ mol^{-1} and 102.0 kJ mol^{-1}, respectively. The average E_a^2 value is 102 ± 1 kJ mol^{-1}. For α higher than 50% the activation energy is different. Its approximate value for α values from 60% to 90% is 126 kJ mol^{-1}. This value was determined on the basis of the TG curve at $\beta = 1,2,5$ K min^{-1}.

X-ray data were collected for CuTPP + benzene with stoichiometries: 4:4, 4:3 and for CuTPP not containing solvent molecules. The X-ray measurements for CuTPP + benzene with stoichiometry 4:3 was preceded by test of stability of this compound at room temperature. This was done as follows. The compound was heated at a rate $\beta = 10$ K min^{-1} to the temperature $T_f^* = 408.5$ K and then quickly cooled in argon atmosphere. For the thus prepared sample many powder X-ray diffraction diagrams were taken for around 3h. The positions and the intensities of the peaks did not change. Moreover, at a heating rate $\beta = 10$ K min^{-1} a DSC measurement was done over the full temperature range. No heat effect corresponding to the first stage was

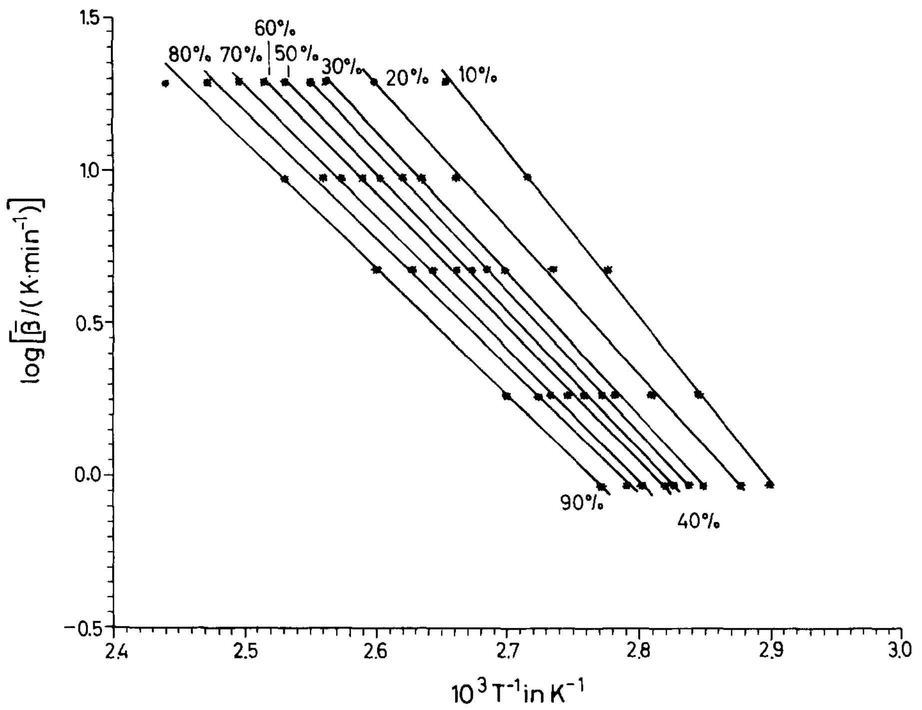


Fig. 3. The dependence of log(β) versus T^{-1} for the first stage CuTPP + benzene desolvation for different fractional extent of reaction, α.

present, whereas the effect of the second stage was observed. Fig. 4 shows the X-ray diagrams obtained for the following compounds: initial with stoichiometry 4:4—(A); with stoichiometry 4:3—(B); not containing solvent molecules—(C). The results of identification of the reflection planes of the first 20 peaks are given in Table 2. The unit cell parameters are:

A. $a = 18.03(0.18)$ Å; $b = 16.94(0.17)$ Å; $c = 16.08(0.16)$ Å
$\alpha = \beta = 90°$; $\gamma = 114.9°$; $V = 4185$ Å^3
B. $a = 15.54(0.16)$ Å; $b = 13.46(0.13)$ Å; $c = 12.13(0.12)$ Å
$\alpha = 90°$; $\beta = 118.4°$; $\gamma = 108.4°$; $V = 2020$ Å^3
C. $a = 13.36(0.13)$ Å; $b = 11.84(0.12)$ Å; $c = 14.24(0.14)$ Å
$\alpha = 116.1°$; $\beta = 110.5°$; $\gamma = 94°$; $V = 1600$ Å^3

Flescher et al. [4] measured the CuTPP monocrystal obtained from benzene solution getting: $a = b = 15.04(0.02)$ Å; $c = 13.993(0.004)$ Å; $\alpha = \beta = \gamma = 90°$; space group I_{42d}; $Z = 4$; $V = 3165$ Å^3. These results are different than those presented above. The cause of the differences is most probably the different way of obtaining the monocrystal. Fleischer et al. produced their monocrystals by slow evaporation of solvent (several months), whereas the authors of this paper obtained the monocrystals by extended heating of the solvated metallocomplex. Without doubt the extended

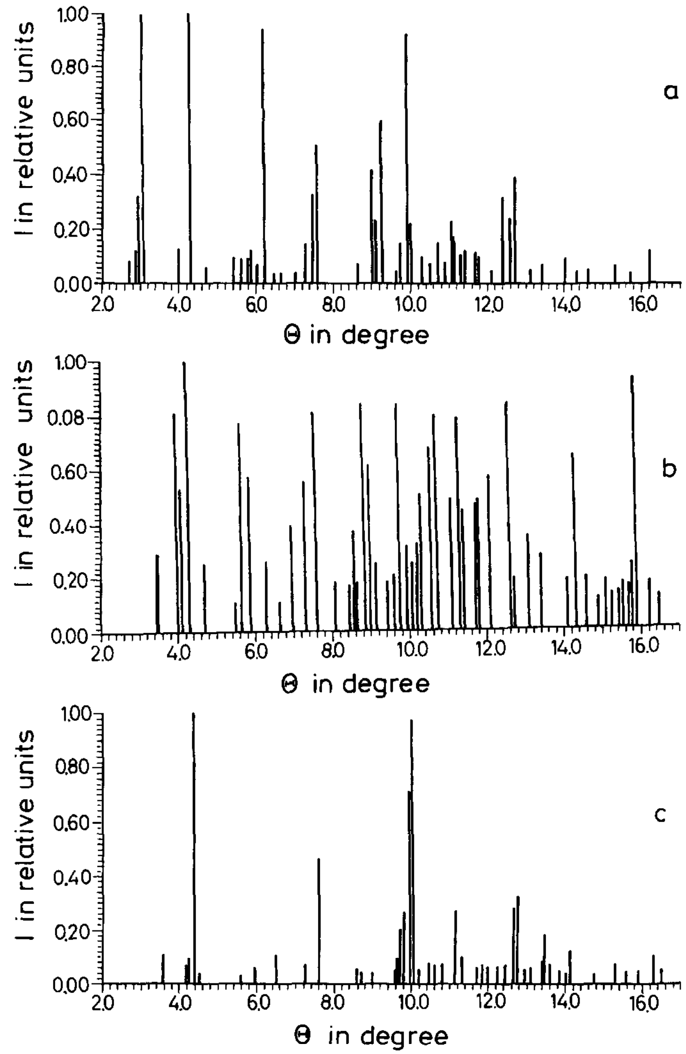


Fig. 4. The powder X-ray diffraction diagrams obtained for CuTPP + benzene with stoichiometry 4:4 (a), 4:3 (b) and 4:0 (c).

heating can cause severe strains leading to defects and finally to the change of crystal symmetry from tetragonal to triclinic. The authors of Ref. [4] calculated the volume of CuTPP cell in the crystal with the space group I_{42d} as equal to $V = 791$ Å^3 whereas in our study $V = 1600/2 = 800$ Å^3. It should also be taken into account that the tetraphenylporphyrins are conformationally flexible and that this can result in different crystal packings depending on the growth conditions.

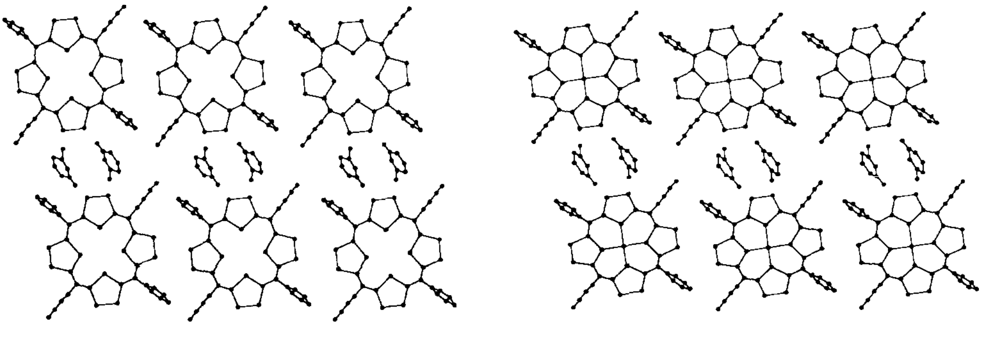
Our structural data were also compared with those obtained for CuTPP + 2(*m*-xylene) [2], for which the following crystal cell parameters were obtained: $a = 13.528$ Å;

Table 2
The experimental, $(d/n)_e$ in Å, and theoretical, $(d/n)_t$ in Å, values of the distance between planes of reflection; the intensity, I in relative units, and the indices, (hkl), for first 20 reflections

4CuTPP + 4benzene (A)					4CuTPP + 3benzene (B)				CuTPP (C)			
N	$(d/n)_e$	$(d/n)_t$	I	(hkl)	$(d/n)_e$	$(d/n)_t$	I	(hkl)	$(d/n)_e$	$(d/n)_t$	I	(hkl)
1	16.36 ± 0.15	16.36	0.08	(100)	12.77 ± 0.15	12.77	0.29	(100)	12.45 ± 0.15	12.45	0.11	(100)
2	15.37 ± 0.15	15.37	0.11	(010)	12.57 ± 0.15	12.57	0.29	(010)	10.59 ± 0.15	10.52	0.07	(010)
3	15.10 ± 0.15	15.10	0.32	(001)	11.05 ± 0.15	10.98	0.81	$(10\bar{1})$	10.46 ± 0.15	10.45	0.09	$(1\bar{1}0)$
4	14.60 ± 0.15	14.70	1	$(1\bar{1}0)$	10.78 ± 0.15	10.83	0.53	$(1\bar{1}0)$	10.16 ± 0.15	10.16	1	(001)
5	11.05 ± 0.15	11.10	0.13	(101)	10.34 ± 0.15	10.34	1	(001)	9.77 ± 0.15	9.74	0.04	$(01\bar{1})(10\bar{1})$
6	10.28 ± 0.15	10.40	1	$(1\bar{1}1)$	9.59 ± 0.08	9.67	0.25	$(\bar{1}11)$	7.92 ± 0.08	7.85	0.03	$(1\bar{1}1)$
7	9.41 ± 0.08	9.40	0.06	(110)	8.04 ± 0.08	7.99	0.11	(011)	7.43 ± 0.08	7.50	0.06	$(11\bar{1})$
8	8.19 ± 0.08	8.18	0.10	(200)	7.83 ± 0.08	7.81	0.77	(110)	6.81 ± 0.08	6.83	0.11	$(101)(\bar{1}11)$
9	7.90 ± 0.08	7.98	0.09	(111)	7.52 ± 0.08	7.46	0.57	$(\bar{2}11)$	6.11 ± 0.08	6.10	0.07	(011)
10	7.66 ± 0.08	7.68	0.10	$(2\bar{1}1)(020)$	7.08 ± 0.08	7.16	0.26	$(20\bar{1})$	5.83 ± 0.05	7.82	0.46	$(02\bar{1})(\bar{2}11)$
11	7.56 ± 0.08	7.55	0.13	(002)	6.66 ± 0.08	6.64	0.11	$(101)(2\bar{1}0)$	5.15 ± 0.02	5.14	0.05	$(21\bar{1})$
12	7.34 ± 0.08	7.35	0.08	$(2\bar{2}0)(1\bar{2}1)$	6.37 ± 0.08	6.39	0.39	$(200)(1\bar{1}1)$	5.10 ± 0.02	5.08	0.04	(002)
13	7.19 ± 0.08	7.19	0.94	(201)	6.16 ± 0.08	6.23	0.55	$(\bar{1}21)$	4.93 ± 0.02	4.93	0.04	$(2\bar{2}1)$
14	6.86 ± 0.08	6.86	0.04	(102)(021)	5.87 ± 0.05	5.86	0.81	$(10\bar{2})(\bar{2}21)$	4.63 ± 0.02	4.63	0.05	(201)
15	6.66 ± 0.08	6.61	0.04	$(2\bar{2}1)$	5.48 ± 0.05	5.49	0.18	$(111)(20\bar{2})$	4.61 ± 0.02	4.61	0.09	$(210)(1\bar{2}2)$
16	6.30 ± 0.08	6.22	0.04	(210)	5.16 ± 0.02	5.16	0.17	$(002)(\bar{3}11)$	4.56 ± 0.02	4.56	0.20	$(3\bar{1}0)(21\bar{2})$
17	6.09 ± 0.08	6.04	0.15	(120)	5.10 ± 0.02	5.08	0.37	(210)	4.52 ± 0.02	4.50	0.26	$(\bar{3}11)$
18	5.95 ± 0.05	6.00	0.33	$(3\bar{1}0)$	5.04 ± 0.02	5.04	0.18	$(120)(11\bar{2})$	4.46 ± 0.02	4.46	0.71	$(12\bar{2})$
19	5.87 ± 0.05	5.89	0.51	(112)	4.93 ± 0.02	4.91	0.83	$(12\bar{1})$	4.44 ± 0.02	4.45	0.98	$(\bar{1}21)(30\bar{1})$
20	5.14 ± 0.02	5.13	0.08	(301)(030)	4.84 ± 0.02	4.83	0.61	$(30\bar{1})(\bar{2}22)$	4.35 ± 0.02	4.34	0.05	$(\bar{1}12)$

$b = 19.098$ Å; $c = 11.98$ Å; $\alpha = 126.29°$; $\beta = 116.13°$; $\gamma = 109.12$; $V = 2231$ Å. If one relates these data to the same number of molecules in the unit cell and compares them with the data presented here, the value to be compared is $V = 4462$ Å^3 whereas for solvate CuTPP + benzene with stoichiometry 4:4 V is 4185 Å^3 and for 4:3 stoichiometry $V = 4040$ Å^3. There is a clear decrease in volume due to desolvation. It also follows from Refs. [1-3] that monocrystals of tetraphenylporphyrin metallocomplexes MTPP (where $M = Cu^{2+}$; Zn^{2+}; Cd^{2+}) with benzene, toluene and *m*-, *o*-, *p*-xylene are characterized by (according to classification by M.P. Byrn et al. [1-3]) crystal lattice falling to the category "expanded by axis a", where for each MTPP molecule there are two molecules of solvent (Fig. 5). In the case of CuTPP + benzene the stoichiometry is 1:1. This could mean that with the fast growth of CuTPP + benzene monocrystal when solvent evaporates at $T = 333$ K the lattice defects have no time to relax and initiate the loss of the solvent molecule.

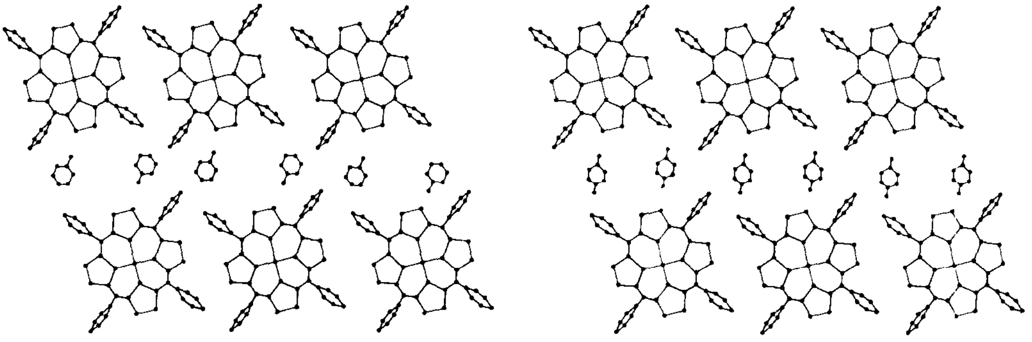
Interesting information was also obtained as a result of thermal and structural studies of H_2TPP + 1,4-dioxane. The TG and DTG curves obtained at diverse heating rates $\beta = 1$, 2, 5 and 10 K min^{-1} in the temperature range 325 to 650 K are shown in Fig. 6 a, b. The general observation is that mass losses occur in two stages extended over a large temperature interval 370 to 650 K. Exact temperature values characterizing DTG curves, like that for the CuTPP solvate, depend on heating rate. The DTG peak relating to the first stage of mass loss is observed in the temperature range 370 to 520 K. The end of the first stage overlaps with the beginning of the second. This overlapping is manifested by the non-zero value of the rate of mass loss between the two peaks. The second part of the DTG curve has an irregular shape with sharp peaks (Fig. 6a, b) and reveals the complex dynamics of processes in this phase of desolvation. When comparing temperatures of maxima of DTG (473 and 558 K) and minima of DSC curves (466 and 560 K), the correspondence of mass losses and endothermal heat effects can be noticed (Fig. 6b). The overlapping of the two stages of desolvation is confirmed by very poor separation of the heat effects.



$2H^{+}$ (m-Xylene)$_2$

Cu^{+2}(m-Xylene)$_2$

Fig. 5. A section parallel to the *a* and *b* axes for metallocomplexes of tetraphenylporphyrin sponges with 2:1 guest: host stoichiometry [1-3].



Zn^{+2}(Toluene)$_2$

Zn^{+2}(p-Xylene)$_2$

Fig. 5b

After the first desolvation stage the stoichiometry of the compound changes from 12:5 to 12:2 (Table 1). The activation energies for this stage calculated for $\alpha = 20\%$; 30%; 40%; 50% are equal to $E_a^1 = 81.7$ kJ mol^{-1}; 79.5 kJ mol^{-1}; 80.1 kJ mol^{-1}; 81.6 kJ mol^{-1}, respectively. The mean activation energy corresponds to $\bar{E}_a^1 = 81 \pm 1$ kJ mol^{-1}. This value is not significantly different for the first desolvation stage of CuTPP + benzene. The γ values ($K = \gamma \exp(-E_a/kT)$, where K is the reaction rate constant), however, differ significantly for CuTPP + benzene and H_2TPP + 1,4-dioxane and are equal to $\gamma = 10^{10}$ min^{-1} and 10^8 min^{-1}, respectively. This shows the different nature of interactions of the solvent molecules with their environment. The complex character of the curves in temperature range 470 to 650 K made distinguishing of the desolvation stages impossible. We have, therefore, applied common description for the period in which the stoichiometry changes from 12:2 to 12:0. Also, the activation energy could not be determined. The heat effect of desolvation of the whole process from 12:5 to 12:0 corresponds to 27.9 kJ (mol H_2TPP)$^{-1}$. The course of changes of heat effect did not justify division of this value between individual stages. The determined heat effect is greater than that obtained for CuTPP + benzene solvate.

The X-ray structural studies were carried out for H_2TPP + 1,4-dioxane solvate of stoichiometry 12:5 and H_2TPP polycrystals of stoichiometry 12:0. Structural studies were not possible for H_2TPP polycrystals having 12:2 stoichiometry as lattice parameters could not be obtained using the algorithm of Ito [11]. This is probably due to phase-mixing effects. The parameters for the solvate of stoichiometry 12:5 (A) are in full agreement with those obtained previously [12,13]. The corresponding data for H_2TPP polycrystal at 298 K corresponds to (B). The results of the identification of the reflection planes of the first 20 peaks are given in Table 3 and Fig. 7. The unit cell parameters are:

A. $a = 25.85(0.25)$ Å; $b = 13.82(0.14)$ Å; $c = 29.42(0.30)$ Å
$\alpha = 132.4°$; $\beta = 90°$; $\gamma = 130.8°$; $V = 6460$ Å^3
B. $a = 16.54(0.17)$ Å; $b = 16.84(0.17)$ Å; $c = 15.28(0.15)$ Å
$\alpha = 120.7°$; $\beta = 110.3°$; $\gamma = 121.4°$; $V = 3069$ Å^3

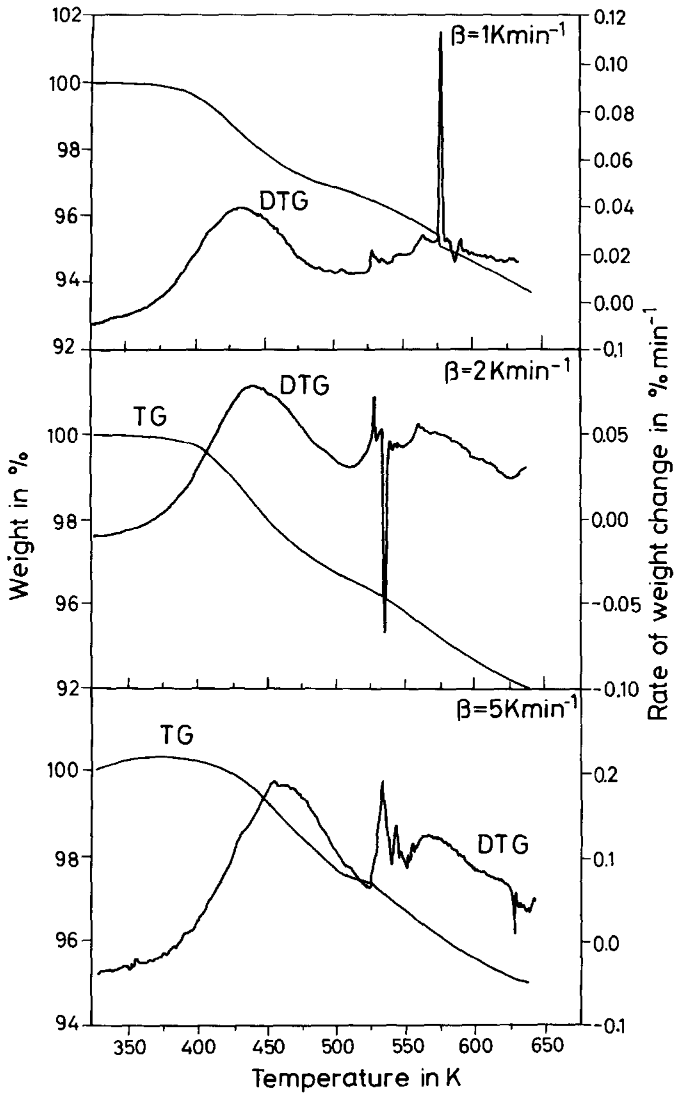


Fig. 6. Thermal behaviour of solvates H_2TPP + 1,4-dioxane. (a) TG and DTG curves for heating rates 1, 2 and 5 K min^{-1}; (b) TG, DTG and DSC curves for $\beta = 10$ K min^{-1}.

The objective of DSC measurements for the polycrystals was to observe their changes during heating and cooling. These studies were carried out in the temperature range 298 to 623 K at the heating rate $\beta = 10$ K min^{-1}. It has been found that there is an endothermic effect between 558 and 597 K, with the greatest heat power at the temperature of 597 K. After fast cooling of the sample the DSC measurement was

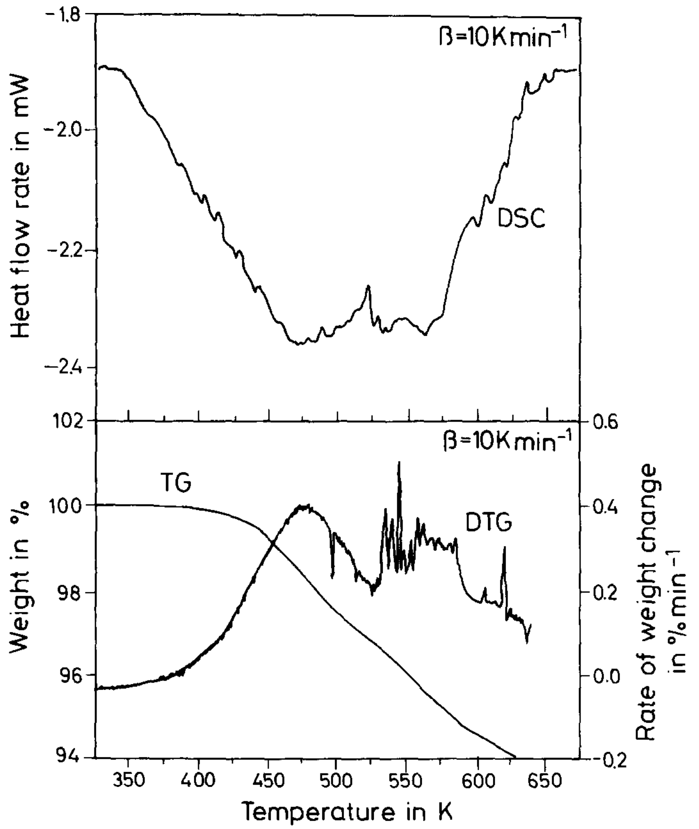


Fig. 6b

repeated, showing a slightly smaller effect. Repeated heating–cooling cycles enable the conclusion that only after the third cycle does one get a value of the heat effect which is reproducible in the next cycles and equal to 400 J mol^{-1}. For the first cycle this value was 1100 J mol^{-1}, for the second it is 800 J mol^{-1}. The X-ray measurements for the polycrystal of H_2TPP without molecules of 1,4-dioxane (C) were also carried out at 603 K in an argon atmosphere. The following data were obtained (cf. Table 3 and Fig. 7):

C. $a = 15.56(0.16)$ Å; $b = 16.81(0.17)$ Å; $c = 15.32(0.15)$ Å
$\alpha = 120.3°$; $\beta = 102.4°$; $\gamma = 115.7°$; $V = 3048$ Å^3

It follows that the unit cell volumes of (B) and (C) are almost the same in both cases, there is also very little difference in geometries. However the peak intensities and their distribution differ considerably. This is probably due to a complex selection rules for the primitive elementary cell.

To see whether the observed heat effects are dependent on the procedure used to obtain the polycrystals we performed the DSC measurements on H_2TPP polycrystals

Table 3
The experimental, $(d/n)_e$ in Å, and theoretical, $(d/n)_t$ in Å, values of the distance between planes of reflection; the intensity, I in relative units, and the indices, (hkl), for first 20 reflections

	H_2TPP (B)				H_2TPP (C)			
N	$(d/n)_e$	$(d/n)_t$	I	(hkl)	$(d/n)_e$	$(d/n)_t$	I	(hkl)
1	14.03 ± 0.15	14.03	0.14	(100)	14.03 ± 0.15	14.03	0.10	(100)
2	13.81 ± 0.15	13.82	0.14	$(1\bar{1}0)$	13.39 ± 0.15	13.39	0.14	(010)
3	13.09 ± 0.15	13.09	0.21	(010)	13.09 ± 0.15	13.05	0.19	$(01\bar{1})$
4	12.72 ± 0.15	12.73	0.92	$(01\bar{1})$	12.90 ± 0.15	12.86	0.47	$(1\bar{1}0)$
5	12.19 ± 0.15	12.19	0.19	(001)	12.62 ± 0.15	12.62	0.87	(001)
6	11.33 ± 0.15	11.35	0.09	$(10\bar{1})$	10.55 ± 0.15	10.58	0.25	$(10\bar{1})$
7	10.16 ± 0.15	10.20	0.51	$(1\bar{1}1)$	8.67 ± 0.08	8.72	0.12	$(11\bar{1})$
8	8.89 ± 0.08	8.81	0.08	$(11\bar{1})$	8.50 ± 0.08	8.52	0.10	(101)
9	8.38 ± 0.08	8.36	0.12	$(\bar{1}11)$	8.23 ± 0.08	8.19	0.10	$(1\bar{2}1)$
10	8.19 ± 0.08	8.22	0.09	$(1\bar{2}1)(2\bar{1}0)$	8.10 ± 0.08	8.09	0.10	(110)
11	7.93 ± 0.08	7.94	0.06	(101)	7.50 ± 0.08	7.49	0.83	(011)
12	7.76 ± 0.08	7.76	0.05	(110)	6.81 ± 0.08	6.78	0.12	$(2\bar{1}1)(20\bar{1})$
13	7.56 ± 0.08	7.61	0.06	$(02\bar{1})$	6.56 ± 0.08	6.55	0.11	$(2\bar{2}1)(02\bar{2})$
14	7.26 ± 0.08	7.26	0.45	$(20\bar{1})(011)$	6.44 ± 0.08	6.44	0.26	$(\bar{2}11)(1\bar{1}2)$
15	7.02 ± 0.08	7.01	0.06	$(200)(01\bar{2})$	6.42 ± 0.08	6.43	0.36	$(1\bar{2}2)(2\bar{2}0)$
16	6.71 ± 0.08	6.65	0.12	$(11\bar{2})$	6.36 ± 0.08	6.31	0.36	(002)
17	6.49 ± 0.08	6.47	0.34	$(10\bar{2})(020)$	5.76 ± 0.05	5.78	1	$(111)(21\bar{1})$
18	6.35 ± 0.05	6.37	0.11	$(02\bar{2})$	5.50 ± 0.05	5.51	0.12	$(12\bar{2})$
19	5.98 ± 0.05	6.03	0.15	$(1\bar{1}2)$	5.44 ± 0.05	5.43	0.10	$(\bar{1}21)$
20	5.63 ± 0.05	5.67	0.57	$(20\bar{2})(1\bar{3}1)$	5.28 ± 0.05	5.27	0.29	$(1\bar{3}2)(20\bar{2})$

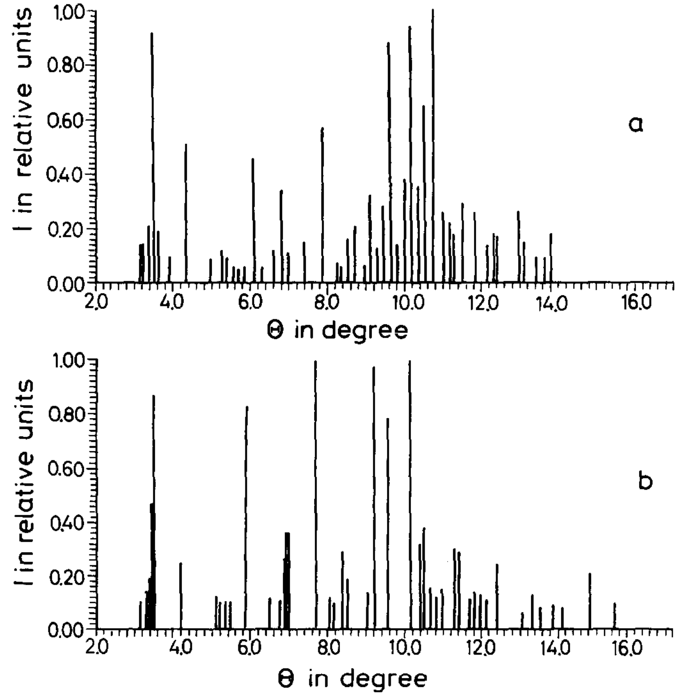


Fig. 7. The powder X-ray diffraction diagrams obtained for H_2TPP at T = 298 K (a) and T = 603 K (b).

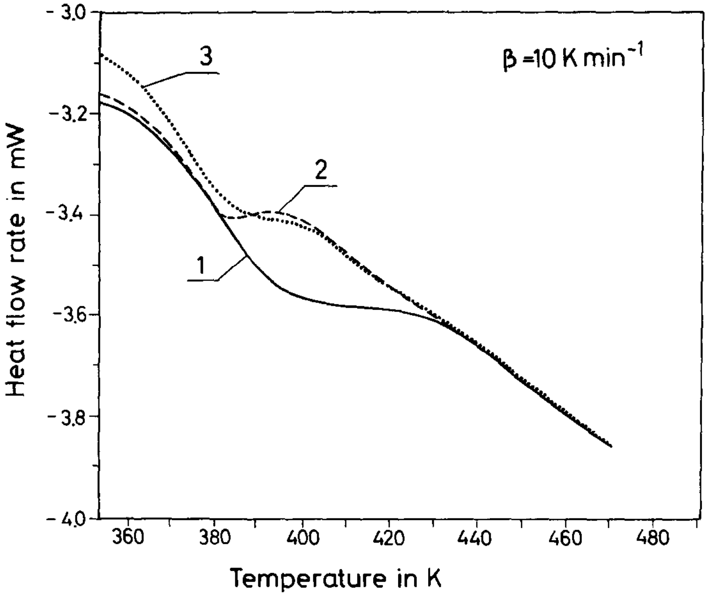


Fig. 8. The DSC curves for H_2TPP polycrystals obtained by sublimation after three heating–cooling cycles.

obtained by sublimation. The results are presented in Fig. 8. The figure shows endothermic effects in the temperature range 369 to 429 K. The values of 971 J mol^{-1}; 462 J mol^{-1} and 340 J mol^{-1} are in a good agreement with those obtained previously. This enables the conclusion that the presence of these effects is not caused by the desolvation process.

It is interesting to note that the crystals of H_2TPP obtained both by sublimation and crystallization from 1,4-dioxane melted at 719 K ($\beta = 10$ K min^{-1}). The heat effect of this phase transition is 41 kJ mol^{-1}.

4. Conclusion

The desolvation processes of CuTPP + benzene and H_2TPP + 1,4-dioxane proceed in two independent stages: the first has ordinary function dependence of mass losses and the second stage has complex character. These facts lead to the conclusion that there are at least two varieties of different positions for molecules of solvent within the crystalline lattice. From X-ray measurements we found that there is a small decrease in the value of volume for the same number of CuTPP molecules in the unit cell, due to desolvation. The symmetry of the crystalline lattice changed from monoclinic to triclinic. There is a reversible thermal effect for crystals of H_2TPP obtained both by sublimation and by crystallization from 1,4-dioxane. These crystalline modifications of H_2TPP melted at 719 K with a heat effect of 41 kJ mol^{-1}.

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