

# Spectral Characteristics and Solvation of Tetrakis(3,5-di-*tert*-butylphenyl)porphine and its Complexes with Some *d* Metals

Elena V. Antina,<sup>a@</sup> Elena V. Balantseva,<sup>b</sup> and Mikhail B. Berezin<sup>a</sup>

<sup>a</sup>*Institute of Solution Chemistry of Russian Academy of Sciences, 153045 Ivanovo, Russia*

<sup>b</sup>*Ivanovo State University of Chemistry and Technology, 153000 Ivanovo, Russia*

@Corresponding author E-mail: [eva@isc-ras.ru](mailto:eva@isc-ras.ru)

*An influence of structural factors and surrounding features on both spectral and enthalpy characteristics of the dissolution and solvation processes and the thermodynamic stability of tetrakis(3,5-di-*tert*-butylphenyl)porphine (H<sub>2</sub>P) and its coordination compounds with a number of *d*-metals have been studied in different solvents using spectroscopic and calorimetric methods. The contribution of  $\pi$ - $\pi$ -interaction of H<sub>2</sub>P ([MP]) - benzene to the solvation process was estimated. It has been shown that  $\pi$ - $\pi$ -stacking interaction between aromatic systems of [MP] and benzene molecules is in the following sequence: [PdP] < [CdP] < [NiP] < [ZnP] < [CuP] < [AgP] < [CoP]. The stability of [MP] increases in the row: [HgP] < [CdP] < [ZnP] < [AgP] < [CuP] < [NiP]  $\approx$  [CoP] < [PdP], which is in agreement with spectral criterion of strength. The coordination unsaturation of metal porphyrins follows the sequence: [(Ac)FeP] < [NiP] < [PdP] < [CoP] < [CdP] < [ZnP] < [CuP] < [AgP] < [HgP] < [(Ac)MnP].*

**Keywords:** Tetrakis(3,5-di-*tert*-butylphenyl)porphine, solution calorimetry, spectral characteristics, complexes with *d* metals, solvation process.

## Introduction

Very often it is difficult to interpret the results obtained for porphyrins, their metal complexes and processes of axial coordination in metalloporphyrins, because the data on specific interaction features between the compounds of this type and solvate molecules are absent. The special emphasis under investigation of the solvation processes is devoted to a correct choice of reference system (porphyrin – “standard” solvent). The main requirement to this system is a solvation of solute only by universal interactions forces. As a rule, benzene or its alkyl derivatives, for instance, a toluene and xylene are used as a “standard” solvent in calorimetric and spectroscopic methods. However, the results of X-ray diffraction and thermogravimetric analysis obtained for the porphyrin crystals which were precipitated from saturated “standard” solvents show that such “standard” is not always “inactive” and in some cases can form stable solvate structures with tetrapyrrole macrocycles.<sup>[1-4]</sup> Such behaviour of a “standard” solvent leads to the incorrect estimations of properties, for example, inaccuracy may occur in case of evaluating the metalloporphyrin coordination unsaturation in compliance with the axial coordination enthalpies  $\Delta a.c.H^0$  obtained *via* thermochemical approach.<sup>[5]</sup>

It seems more desirable to use paraffin hydrocarbons like a “standard” medium surroundings. However, the majority of macrocyclic tetrapyrroles have poor solubility in these solvents. Increase of solubility of porphyrins in nonpolar solvents by introduction of alkyl bulky substituents should not significantly distort<sup>[5]</sup> the general pattern of “structure - property” relationship. Therefore, here we have selected the tetrakis(3,5-di-*tert*-butylphenyl)

porphine (H<sub>2</sub>P) and its coordination compounds as objects of our work. Due to their high solubility in the media of different nature we were able to use cyclohexane as a reference solvent having universal solvating properties.<sup>[6-8]</sup>

## Experimental

The synthesis, methods of purification and the spectral properties (<sup>1</sup>H NMR, EPR) of some H<sub>2</sub>P and [MP] (M=Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>, Pd<sup>II</sup>, Ag<sup>II</sup>, Cd<sup>II</sup>, Hg<sup>II</sup>) as well as [(Ac)MP] (M=Fe<sup>III</sup>, Mn<sup>III</sup>) were previously published by our working group.<sup>[7,9]</sup>

The crystal samples of metalloporphyrins were dried under low pressure at 353-363 K during 24 h or more up to a moment when the weight of sample was constant. The solvents (pyridine, benzene, chloroform, and cyclohexane) used in experiments were the highly purified commercial products. All the solvents were treated additionally to remove the impurity and a rest of water using the known methods.<sup>[10]</sup> The water content of the solvent was determined by Karl Fischer titration and did not exceed 0.02 %.

The data of solution enthalpies ( $\Delta solH^0$ ) of H<sub>2</sub>P and [MP] have been obtained on isoperibolic calorimeter at 298.15 K. It should be noted that there are no data on the enthalpy of crystal lattice and enthalpy of conformational changes, which can appear in transfer of substance from solid to liquid phase. Taking this fact into account to discuss the results obtained in calorimetric experiments we used the values of transfer enthalpy from the reference solvent (cyclohexane) to the studied solvent which were calculated using the following Equation (1):

$$\Delta trH^0 = \Delta solH_i^0 - \Delta solH_{st}^0 \quad (1),$$

where  $\Delta solH_i^0$  and  $\Delta solH_{st}^0$  are the changes of enthalpy during dissolution of the compound in the studied and reference solvent, correspondingly. Analysis of coordination properties of [MP] toward electron donating pyridine molecules have been carried out

using the enthalpies of axial coordination ( $\Delta a.c.H^0$ ) estimated from the Equation (2):

$$\Delta a.c.H^0 = \Delta trH_{MP}^0 - \Delta trH_{H_2L}^0 \quad (2),$$

where  $\Delta trH_{MP}^0$  and  $\Delta trH_{H_2L}^0$  are the transfer enthalpies of the complex and the ligand in the studied solvent, correspondingly.

The visible spectra of samples have been measured on Specord M 40 spectrophotometer within 350 – 700 nm region.

## Results and Discussion

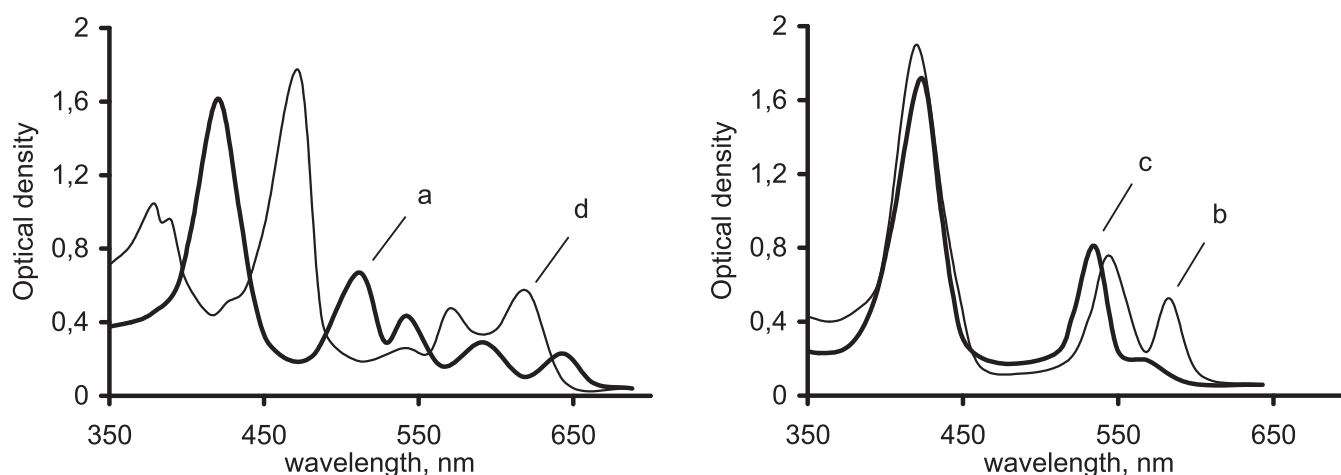
The spectral characteristics of  $H_2P$  and its coordination compounds with *d* metals in some organic solvents are presented in Tables 1 and 2. It is known<sup>[11]</sup> that there are few main types of porphyrin spectra which are determined by the number and intensity of spectral bands. As it is possible to see from the Tables 1,2 and Figure 1  $H_2P$  has ethio-type of spectrum (Figure 1a) in all studied solvents.

**Table 1.** Values ( $\lambda$ , nm) and logarithm of molar absorptivity ( $lg\epsilon$ ) of spectral bands for the tetrakis(3,5-di-*tert*-butylphenyl)porphine and its metal complexes in organic solvents.

Solvent	$\lambda$ , $lg\epsilon$																	
	$H_2P$		[CoP]		[NiP]		[CuP]		[ZnP]		[PdP]		[AgP]		[CdP]		[HgP]	
$C_6H_{12}$	651	3.12																
	595	3.14	567	<i>sh</i>	618	3.37	570	<i>sh</i>	620	<i>sh</i>	601	3.45	583	<i>sh</i>	616	3.69	599	<i>sh</i>
	548	3.35	527	5.19	529	4.10	539	5.59	546	4.19	523	4.32	543	4.19	548	5.14	551	3.68
	514	3.55																
	415	4.51	412	6.13	418	4.54	416	6.25	421	4.67	418	4.52	427	4.52	419	6.31	428	4.60
$C_6H_6$	633	3.97																
	586	4.06	576	<i>sh</i>	608	3.62	560	<i>sh</i>	581	3.90	597	3.87	557	<i>sh</i>	602	3.97	618	4.06
	545	4.14	523	4.17	522	4.39	533	4.42	545	4.41	520	4.50	536	4.30	562	4.06	573	4.09
	511	4.35																
	417	5.35	412	5.18	415	5.33	415	5.44	420	5.28	416	5.38	423	4.98	433	4.76	431	5.08
$CHCl_3$	639	4.01															-	-
	586	3.97	572	<i>sh</i>	610	3.59	558	<i>sh</i>	581	4.01	597	3.97	562	<i>sh</i>	603	4.04		
	547	4.16	523	4.62	524	4.38	535	4.30	545	4.43	520	4.69	538	4.51	562	4.11		
	513	4.37																
	416	5.46	411	5.72	416	5.40	415	5.28	419	5.43	412	5.27	422	5.07	432	5.19		
$C_5H_5N$	639	3.86																
	586	3.77	597	<i>sh</i>	608	3.70	570	<i>sh</i>	597	4.27	597	3.77	561	<i>sh</i>	605	4.10	622	4.04
	547	3.99	529	3.85	524	4.35	538	4.26	559	4.39	519	4.43	538	4.37	562	4.19	578	4.13
	513	4.23																
	417	5.31	411	5.06	417	5.36	419	5.31	427	5.34	416	5.20	425	5.22	431	5.37	437	4.97

**Table 2.** Values ( $\lambda$ , nm) and logarithm of molar absorptivity ( $lg\epsilon$ ) of spectral bands for the complexes of tetrakis(3,5-di-*tert*-butylphenyl)porphine with ions of *d*-metals in organic solvents.

Solvent	$\lambda$ , $lg\epsilon$								Solvent	$\lambda$ , $lg\epsilon$							
	[(Ac)MnP]		[(Ac)FeP]		[(Cl)FeP]		[(FeP) <sub>2</sub> O]			[(Ac)MnP]		[(Ac)FeP]		[(Cl)FeP]		[(FeP) <sub>2</sub> O]	
$C_6H_{12}$	614	4.95	690	3.44	683	3.50	628	3.37	$CHCl_3$	618	4.98	710	<i>sh</i>	687	<i>sh</i>	-	
	577	4.95	650	<i>sh</i>	675	<i>sh</i>	573	4.10		581	4.96	590	<i>sh</i>	667			
	523	4.76	575	3.59	585	<i>sh</i>				528	4.82	569	<i>sh</i>	587	<i>sh</i>		
	477	5.85	514	3.90	506	3.88	414	4.54		466	5.85	516	3.50	514			
	412	5.45	421	4.20	422	5.15				410	<i>sh</i>	419	5.16	419			
	383	5.60	386	3.94	365	3.83				386	5.60	364	<i>sh</i>	385			
$C_6H_6$	613	4.97	700	<i>sh</i>	680	3.52	615	4.18	$C_5H_5N$	636	4.91	710	<i>sh</i>	716		627	4.02
	577	4.95	660	<i>sh</i>	675	<i>sh</i>	573	4.34		615	4.90	590	<i>sh</i>	668	<i>sh</i>	573	4.81
	526	4.80	568	3.70	585	<i>sh</i>	514	<i>sh</i>		579	4.76	564	<i>sh</i>	606	<i>sh</i>	514	<i>sh</i>
	472	5.85	510	<i>sh</i>	504	3.92	417	5.45		525	4.30	532	3.50	513		421	5.23
	388	5.40	415	5.35	419	5.18				476	5.85	427	5.16	422			
	374	5.60	364	<i>sh</i>	372	3.85				406	<i>sh</i>	364	<i>sh</i>				
								386	4.40								



**Figure 1.** Absorption spectra of some compounds in benzene: a)  $H_2P$ ; b)  $[ZnP]$ ; c)  $[AgP]$ ; d)  $[(Ac)MnP]$ .

This spectral type is characteristic for the most of porphyrin derivatives.<sup>[11-12]</sup> Hypsochromic shift (-) of the first band during transfer of  $H_2P$  from cyclohexane to the other solvents ( $\Delta\lambda_{\max}^I = \lambda_{\max}^I - \lambda_{\max, C_6H_{12}}^I$ ) is distinctly higher in benzene (-18 nm) in comparison to pyridine and chloroform (-12 nm).

Among the investigated coordination compounds with  $d$  metals the complexes of palladium(II), nickel(II), copper(II), cobalt(II), and silver(II) show the spectra of “hypso-type”, the complexes of zinc(II), mercury(II), and cadmium(II) show “normal-type”, whereas  $[(Ac)FeP]$  and  $[(Ac)MnP]$  demonstrate the “hyper-type” spectra.

It was revealed that the transfer of  $Zn^{II}$ ,  $Cd^{II}$ , and  $Hg^{II}$  complexes to cyclohexane from the other solvents was accompanied by a mostly intensive hypsochromic effect of the long-wave band ( $\lambda_{\max}^I$ ). This leads to conversion of “normal-type” spectrum to “hypso-type” spectrum (Figure 1b,c) and could be caused by a lesser auxo influence on  $\pi$ -system of the chromophore by the metal ions with electronic configuration  $d^{10}$  as compared to the metals with incomplete  $3d$  sub-shell. We have to remind that ions with configuration  $(n-1)d^{10}ns^0$  are able to react with porphyrin ligands only through  $\sigma$ -type coordinating interaction, whereas ions with incomplete  $(n-1)d$  sub-shell can coordinate porphyrin ligand by both  $\sigma$ - and  $\pm \pi$ -dative interactions. This effect of electronic structure of metal ion is difficult to detect in aromatic (benzene, pyridine) and proton-donating (chloroform) solvents. These difficulties arise from the solvatochromic effects due to the specific solvation interactions what ultimately reflects in changes of the spectral characteristics of compounds.

Transfer of complexes from the cyclohexane to the polar solvents with more distinct donor-acceptor properties is accompanied by solvatochromic effect with considerable changes of  $\lambda_{\max}^I$  position. The general behavior of  $\Delta\lambda_{\max}^I = \lambda_{\max, i}^I - \lambda_{\max, C_6H_{12}}^I$  changes in the spectra of  $[M^{II}P]$  and  $[(X)M^{III}P]$  solutions is presented in Table 3;  $\lambda_{\max, C_6H_{12}}^I$  and  $\lambda_{\max, i}^I$  are the positions of the long-wave band in cyclohexane and in the investigated solvent, correspondingly.

The sequences are in a good agreement with the case of transfer processes from benzene to chloroform, however for the transfer to pyridine the significant realignment in a position sequence of  $[MP]$  is observed. Transfer of  $[M^{II}P]$  complexes, with the exception of  $[HgP]$  and  $[CoP]$ , are accompanied by hypsochromic shift. Its value is decreased when benzene is replaced by chloroform and by pyridine. The minimal solvatochromic effects are displayed for  $[PdP]$  and  $[NiP]$ . In the case of  $[HgP]$ ,  $[CoP]$ , and  $[(X)M^{III}P]$  complexes the reverse behaviour was revealed. Increase of value of bathochromic ( $+\Delta\lambda_{\max}^I$ ) or hypsochromic ( $-\Delta\lambda_{\max}^I$ ) shift is an evidence of change in chromophore activity of ligand consisting of coordinating compounds. That is caused by amplification or weakening of polarization of chromophore  $\pi$ -system. In general, we can assume that the reason of the observed changes are the solvation contributions from: 1)  $\pi$ - $\pi$ -interactions between the aromatic systems of solvent and  $[MP]$  (during transfer processes to benzene and pyridine); 2) donor-acceptor interactions of  $[MP]$  with the molecules of more polar solvents. Note that changes in the absorption spectra of some complexes in pyridine and chloroform in comparison  $C_6H_{12}$  are due to the sum of two main solvation effects:

**Table 3.** The long-wave band positions in the UV-vis spectra of  $[M^{II}P]$  and  $[(X)M^{III}P]$  in various solvents.

$C_6H_6$ :	[HgP] < [(Ac)FeP] < [CoP] < [(Ac)MnP] < [PdP] < [NiP] = [CuP] < [CdP] < [AgP] < [ZnP],									
$\Delta\lambda_{\max}^I$	+19	+10	+9	+1	-4	-10	-10	-14	-26	-39
$CHCl_3$ :	- [(Ac)FeP] < [CoP] < [(Ac)MnP] < [PdP] < [NiP] < [CuP] < [CdP] < [AgP] < [ZnP],									
$\Delta\lambda_{\max}^I$	+20	+5	+4	-4	-8	-12	-13	-21	-39	
Py:	[CoP] < [HgP] < [(Ac)FeP] < [(Ac)MnP] < [CuP] < [PdP] < [NiP] < [CdP] < [AgP] < [ZnP]									
$\Delta\lambda_{\max}^I$	+30	+23	+22	+1	0	-4	-10	-11	-22	-23

Notice: symbols (+) and (-) correspond to the bathochromic or hypsochromic shift of  $\lambda_{\max}^I$  during the transfer from cyclohexane to the investigated solvent.

$\Delta\lambda^l = \Delta\lambda_{\pi-\pi}^l \pm \Delta\lambda_{ac}^l$ . When these effects have the same direction there is a rise of chromophore activity of  $\pi$ -system, otherwise it is decreased in the case of different directions of the effects.

It is known<sup>[12]</sup> that position of the first absorption band in the spectra of the same type of covalent porphyrin complexes varies symbatically with the stability of the complex supposing that the role of inverse dative  $\pi$ -bonds is slight and we can neglect the distorting factor of the ligand structure. In investigated solvents for all complexes [M<sup>II</sup>P] the value of the shift of the first absorption band is negative as compared to that of the initial ligand ( $\Delta\lambda^l = \lambda_{MP}^l - \lambda_{H_2P}^l$ ) (Table 4). For instance, in the case of [PdP] in cyclohexane the  $\Delta\lambda^l$  value will be calculated as 523 – 651 = –128. It should be noted that for the calculation we used only the well-defined peaks while the shoulders were ignored. According to the spectral criteria of stability  $\Delta\lambda^l$  in cyclohexane, benzene, and chloroform (the solvents which are not able to solvate a complex-forming atom specifically<sup>[13]</sup>) the [M<sup>II</sup>P] complexes form the next row of stability: [HgP] < [CdP] < [ZnP] < [AgP] < [CuP] < [NiP]  $\approx$  [CoP] < [PdP], whereas the stability of complexes of triple-charged metals is decreased upon transfer from [(Ac)MnP] to [(Ac)FeP]. Earlier the similar behavior for some tetraphenylporphyrinates [MTPP] (M = Pd<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, and Zn<sup>II</sup>) was established on a basis of analysis done for the data on spectral criteria.<sup>[12,14]</sup> An exception is [AgP] complex, which is less stable then [AgTPP] probably due to the reducing of inverse dative  $\pi$ -effect of Ag  $\xrightarrow{\pi}$  N coordination owing to the strong +I-induction effect of substituents.

Thereby, an introduction of *tert*-butyl substituents does not have a distinct influence on general character of dependence between the [MTPP] stability and chromophore structure.

The low stability of the mercury(II) complex compared with other complexes of H<sub>2</sub>P is caused by large ionic radius of Hg<sup>2+</sup>. That leads to the weakening of effective coordination interactions between metal and porphyrin resulting from the displacement of metal ion out of macrocycle plane.

The obtained data point out that solvation factors have an essential influence on the state of investigated compounds in solutions. Therefore, it was important to study the peculiarities of solvation by the solvents of different nature using the dissolution calorimetry.

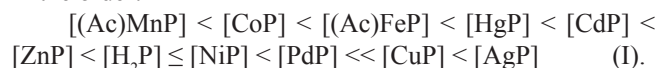
Hypersolubility of the investigated compounds allows to study the thermochemical characteristics of dissolution and solvation by calorimetric method more thoroughly. adue to that we were succeeded in measuring of dissolution enthalpies for H<sub>2</sub>P and some of its coordination compounds in cyclohexane, which displays a predominantly universal type of solvation.

Enthalpy characteristics of these solution processes ( $\Delta\text{solH}^0$ , transfer ( $\Delta\text{trH}^0$ ) and axial coordination ( $\Delta\text{a.c.H}^0_{\text{st}, \text{C}_6\text{H}_{12}}$ ) of the studied compounds in comparison with the available literature data for H<sub>2</sub>TPP and some [MTPP] are collected in Tables 5 and 6. As can be seen the solvation processes of H<sub>2</sub>P and [M<sup>II</sup>P] in chloroform, pyridine, and benzene are more exothermic that that for the unsubstituted analogues.<sup>[4]</sup> It is evident that this phenomenon is induced by the increasing contributions from the universal solvation and weakening of molecular crystal lattice which are caused by the effects of alkyl substitution.<sup>[8,15]</sup>

The dissolution processes of H<sub>2</sub>P and majority of [MP] (except [CoP], [(Ac)MnP], and [(Ac)FeP]) are the most endothermic in cyclohexane. Observable relative difference in  $\Delta\text{solH}^0$  values is a consequence of different rigidity of the crystal lattice of individual substances.

The solvation contribution from  $\pi$ - $\pi$ -stacking interactions H<sub>2</sub>P – solvent that was estimated assuming that  $\Delta\text{trH}^0$  from cyclohexane to benzene and pyridine is identical for the both aromatic solvents and equals –37.8 kJ/mol. Thereby, it is possible to conclude that in pyridine there is no donor-acceptor interactions of the nitrogen atom of Py and proton of the HN< groups of the macrocyclic ligand. It is in agreement with the findings of V.V. Aleksandriiskii and coworkers.<sup>[16]</sup> The comparison of results with the data obtained for H<sub>2</sub>TPP, which forms pyridinium salts, allows to conclude that the observed effect may be associated with the decrease of acidity of the H<sub>2</sub>P ligand due to the +I-electronic effects of the alkyl substituents.

For the of most coordination compounds (excepting [CoP] and [(Ac)M<sup>III</sup>P]) the  $\Delta\text{trH}^0$  values to benzene have been found to be negative and their absolute values are increased in the order:



This sequence demonstrates the improving of conditions for the  $\pi$ - $\pi$ -type solvation process for [CuP] and [AgP] complexes. This inference is in the good agreement with the results of thermogravimetric analysis which demonstrates that [CuP] and [AgP] form the most stable crystal solvates with two C<sub>6</sub>H<sub>6</sub> molecules, whereas [(Ac)MnP] and [HgP] do not reveal any pronounced ability to form crystal solvates with benzene.<sup>[9,17]</sup>

It was found that exothermicity of the transfer processes of compounds from cyclohexane to chloroform is higher than that from cyclohexane to benzene. This can be attributed to the two reasons: 1) improvement of the solvation conditions due to the growth of a polarity and dielectric constant of the solvent; 2) contribution from the donor-acceptor ( $\geq \text{N} \cdots \text{HCCl}_3$ ) interactions. The latter is strongly displayed in the case of

**Table 4.** Spectral criterion of strength  $\Delta\lambda^l$  for [MP] (nm).

Solvent	$\Delta\lambda^l$ , nm									
	PdP	CoP	NiP	CuP	AgP	ZnP	CdP	HgP	(Ac)FeP	(Ac)MnP
C <sub>6</sub> H <sub>12</sub>	-128	-124	-122	-112	-108	-105	-103	-100	39	-37
C <sub>6</sub> H <sub>6</sub>	-113	-110	-111	-100	-97	-88	-71	-60	67	-20
CHCl <sub>3</sub>	-119	-116	-115	-104	-101	-94	-77	-	71	-21

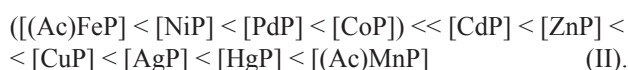


**Table 5.** Enthalpy characteristics of the processes of solution ( $\Delta\text{solH}^0$ ), transfer from cyclohexane ( $\Delta\text{trH}^0$ ) and pyridine axial coordination ( $\Delta\text{a.c.H}^0_{\text{st,C}_6\text{H}_{12}}$ ) obtained for  $\text{H}_2\text{P}$  and [MP] (kJ/mol, 298.15 K).

Compound	$\text{C}_6\text{H}_{12}$		$\text{C}_6\text{H}_6$		$\text{CHCl}_3$		$\text{C}_5\text{H}_5\text{N}$	
	$\Delta\text{solH}^0$	$\Delta\text{solH}^0$	$\Delta\text{trH}^0$	$\Delta\text{solH}^0$	$\Delta\text{trH}^0$	$\Delta\text{solH}^0$	$\Delta\text{trH}^0$	$\Delta\text{a.c.H}^0_{\text{st,C}_6\text{H}_{12}}$
$\text{H}_2\text{P}$	19.7±0.5	-18.1±1.2	-37.8	-35.4±1.2	-55.1	-18.1±1.8	-37.8	-
[ZnP]	26.4±1.2	-6.3±0.5	-32.7	-19.1±1.2	-45.5	-26.4±1.9	-52.8	-15.0
[CoP]	-6.5±1.4	11.2±0.4	17.7	-2.6±0.5	3.9	-46.0±1.0	-39.5	-1.7
[CdP]	43.7±0.8	16.6±0.7	-27.1	-2.5±0.3	-46.2	-3.6±1.0	-47.3	-9.5
[CuP]	28.0±1.1	-25.2±1.7	-53.2	-25.7±1.4	-53.7	-29.3±1.9	-57.3	-19.5
[NiP]	12.2±1.0	-26.2±0.8	-38.4	-44.3±1.9	-56.5	-19.3±1.5	-31.5	6.3
[AgP]	50.2±0.9	-4.0±0.5	-54.2	-21.2±0.8	-71.4	-8.9±0.4	-59.1	-21.3
[PdP]	15.5±1.5	-24.2±1.2	-39.7	-37.1±1.7	-52.6	-21.7±1.6	-37.2	0.6
[HgP]	10.7±0.6	-9.6±0.5	-20.3	-	-	-56.0±1.9	-66.7	-28.9
[(Ac)MnP]	31.0±0.8	50.7±1.8	19.7	30.9±2.0	-0.1	-37.6±1.8	-68.6	-30.8
[(Ac)FeP]	11.9±1.0	27.1±1.0	15.2	-20.7±1.5	-32.6	-16.4±0.7	-28.3	9.5

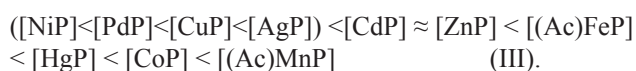
$\text{H}_2\text{P}$ ,<sup>[5]</sup> that is common for the synthetic ligands (including  $\text{H}_2\text{TPP}$ ) and especially for the natural porphyrins.<sup>[18]</sup> In the case of [MP] the contribution from such interactions to the total solvation can increase by even a weak distortion of the planar structure of the coordination center ( $\text{N}_4$ ) caused by the steric effect of the bulky *tert*-butyl substituents.

On the basis of the data presented in Table 5 we have determined the following sequence of complexes in compliance with increasing of the negative values of axial enthalpy  $\Delta\text{a.c.H}^0$  of pyridine calculated using the  $\Delta\text{trH}^0$  from cyclohexane:



Analysis of  $\Delta\text{a.c.H}^0$  values demonstrates a low ability to the additional coordination of the electron-donating molecules among [(\text{Ac})FeP], [NiP], [PdP], [CoP] and an amplification in a coordinating unsaturation for the next complexes of this series. By reason of a low solubility of [MTPP] in cyclohexane the corresponding data for  $\Delta\text{solH}^0$  can not be obtained. Therefore, in Table 6 we present the values of axial coordination enthalpies for the investigated metalloporphyrinates and their analogues which were calculated using the transfer enthalpies from benzene and were termed as ( $\Delta\text{a.c.H}^0_{\text{st,C}_6\text{H}_6}$ ).

In agreement with  $\Delta\text{a.c.H}^0_{\text{st,C}_6\text{H}_{12}}$  values the capability of [MP] to axial coordination grows up in the following sequence:



It is easy to see from the comparison of the rows (II) and (III) that discrepancies in their sequence are strikingly disclosed for compounds which are susceptible to specific molecular  $\pi$ - $\pi$ -complex forming with benzene. The reason of mismatches is that the value of  $\Delta\text{a.c.H}^0_{\text{st,C}_6\text{H}_6}$  in such cases along with a contribution from axial coordination takes into account the compensation energy contribution

from the specific solvation of metalloporphyrins by benzene.

**Table 6.** The axial coordination enthalpies ( $\Delta\text{a.c.H}^0_{\text{st,C}_6\text{H}_6}$ ) of pyridine by metal complexes of  $\text{H}_2\text{P}$ ,  $\text{H}_2\text{TPP}$ ,<sup>[4]</sup>  $\text{H}_2(4\text{'BuPh})_4\text{P}$ <sup>[4]</sup> (298.15 K, kJ/mol).

Compound	$\Delta\text{a.c.H}^0_{\text{st,C}_6\text{H}_6}$	Compound	$\Delta\text{a.c.H}^0_{\text{st,C}_6\text{H}_6}$
[ZnP]	-20.1	[NiP]	6.9
[ZnTPP] <sup>[4]</sup>	-47.3	[NiTPP] <sup>[4]</sup>	-
[Zn(4-'BuPh) <sub>4</sub> P] <sup>[4]</sup>	-36.1	[AgP]	-4.9
[CoP]	-57.2	[PdP]	2.5
[CoTPP] <sup>[4]</sup>	-31.6	[HgP]	-46.4
[CdP]	-20.2	[(Ac)MnP]	-88.3
[CdTPP] <sup>[4]</sup>	-30.0	[(Ac)MnTPP] <sup>[4]</sup>	-27.2
[CuP]	-4.1	[(Cl)MnTPP] <sup>[4]</sup>	-29.7
[CuTPP] <sup>[4]</sup>	1.3	[(Ac)FeP]	-43.5
		[(Ac)FeTPP] <sup>[4]</sup>	-19.2

For instance, the high contribution from the interaction of [AgP] and [CuP] with benzene (Table 5) almost completely compensates the effect of axial coordination of pyridine, that explains the small values of  $\Delta\text{a.c.H}^0_{\text{st,C}_6\text{H}_6}$  for given complexes (row III).

## Conclusions

Thus, due to a higher solubility of the studied compounds we were able to use cyclohexane<sup>[19]</sup> as a standard solvent, which allowed us to identify the ability of [CuP] and [AgP] complexes to the additional coordination of pyridine molecules. This ability would be impossible to discover using the data obtained from analysis of  $\Delta\text{a.c.H}^0_{\text{st,benzene}}$  values. Nevertheless, we would like to underline that in the case of low solubility of porphyrins in aliphatic solvents for the reliable understanding it would be rational to combine the calorimetric data analysis with

thermogravimetric and/or X-ray structure analysis of crystal solvates.

## References

1. Scheidt W.R., Kastner M.E., Hatano K. *Inorg. Chem.* **1978**, *17*, 706-710.
2. Scheidt W.R., Reed C.A. *Inorg. Chem.* **1978**, *17*, 710-716.
3. Kirnes I.F., Reed C.A., Scheidt W.R. *J. Am. Chem. Soc.* **1977**, *99*, 1093-1101.
4. Lebedeva N.Sh., Antina E.V., V'ugin A.I. *Russ. J. Phys. Chem.* **1999**, *73*, 930-934.
5. V'ugin A.I., Antina E.V., Berezin M.B. *Problemy Khimii Rastvorov [The Problems of Solution Chemistry]*. Moskva: Nauka, **1998**. 216 p. (in Russ.).
6. V'ugin A.I., Antina E.V., Berezin M.B., Lebedeva N.Sh., Barrannikov V.P. In: "Solution Chemistry and Technology of the Liquid-phase Materials. Achievements and Future Trends" Ivanovo. **2006**, 86-104. (in Russ.).
7. Balantseva E.V., Antina E.V., Berezin M.B. Deposited 09.04.03. No. 669-B2003, **2003**, 23.
8. Balantseva E.V., Antina E.V., Berezin M.B., V'ugin A.I. *Russ. J. Phys. Chem.* **2004**, *78*, 1435-1438.
9. Balantseva E.V., Antina E.V., Berezin M.B., V'ugin A.I. *Russ. J. Inorg. Chem.* **2005**, *50*, 1566-1570.
10. Gordon A., Ford R. *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*. New York-London-Sydney-Toronto, **1972**. 542 p.
11. Berezin B.D., Enikolopyan N.S. In: *Porfiriny: Struktura, Svoystva, Sintez [Porphyrins: Structure, Properties, Synthesis]* (Enikolopyan N.S., Ed.). Moskva, Nauka, **1985**, 334 p. (in Russ.).
12. Berezin B.D. *Coordination Compounds of Porphyrins and Phthalocyanine*. New Jork-Toronto: J. Wiley, **1981**, 286 p.
13. Berezin D.B. *J. Appl. Spectr.* **1999**, *66*, 521-527.
14. Lomova T.N., Volkova N.I., Berezin B.D. *Zh. Neorg. Khim.* **1987**, *32*, 969-974 (in Russ.).
15. Sugiura K.-I., Iwasaki K., Umishita K., Hino Sh., Ogata G., Miyajima S., Sakata Y. *Chem. Letters* **1999**, *28*, 841-842.
16. Aleksandriiskii V.V., Islyaikin M.K., Burmistrov V.A., Syrbu S.A. *Macroheterocycles* **2009**, *2*, 52-56.
17. Antina E.V., Balantseva E.V., Rummyantsev E.V. In: *Materials of the 61st Calorimetry Conference*, Boulder, Colorado USA, **2006**, 323-324.
18. V'ugin A.I. *Termodinamika Prozessov Rastvoreniya i Solvatatsii Prirodnikh i Sinteticheskikh Porfirinov i ikh Kompleksov, [Thermodynamics of the Solvation and Solvation Processes of the Natural and Synthetic Porphyrins and their Complexes]*, in *Nonelectrolyte Solutions in Liquids* (Nikiforov M.Yu., Al'per G.A., Durov V.A., etc., Eds.). Moskva: Nauka, **1989**, p. 263. (in Russ.).
19. Weissberger A., Proskauer E.S., Riddick J.A., Toops E.E. *Organic Solvents: Physical Properties and Methods of Purification*, Vol. 7 of *Techniques in Modern Chemistry*. Interscience, New York, **1955**; (Russ. transl., Moskva: Inostrannaya Literatura, **1958**).

Received 30.04.2010

Accepted 20.10.2010