Inorganic Chemistry
Article

Inorg. Chem. **2010**, *49*, 659–664 **659**
DOI: 10.1021/ic901921q

Experimental Determination of Enthalpies of Solution of Tetraphenyl Porphyrin (TPP) and Some Metal Derivatives, in Chloroform: Interpretation of the Solvation Processes at a Molecular Level

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Received September 29, 2009

The enthalpies of solution, $\Delta_{sol}H_m$, for 5,10,15,20-tetraphenylporphine (CA registry number 917−23−7, TPP), 5,10,15,20-tetraphenylporphine of Co(II), Ni(II), Cu(II), and Zn(II) (to be written as CoTPP, NiTPP, CuTPP, and ZnTPP) in chloroform, were calorimetrically measured at $T = 298$ K in the concentration ranging from 3.5×10^{-5} to 2.8×10^{-4} $\mathrm{mol \cdot kg^{-1}}$. Through the linear extrapolation of the experimental data, corresponding values at infinite dilution were determined as: $\Delta_{sol}H_m\,(\mathrm{ZnTPP}) = (55.5 \pm 0.2)\ \mathrm{kJ \cdot mol^{-1}}$, $\Delta_{sol}H_m\,(\mathrm{CoTPP}) = (36.9 \pm 0.2)\ \mathrm{kJ \cdot mol^{-1}}$, $\Delta_{sol}H_m\,(\mathrm{TPP}) = (25.7 \pm 0.6)\ \mathrm{kJ \cdot mol^{-1}}$, $\Delta_{sol}H_m\,(\mathrm{NiTPP}) = (15.6 \pm 0.1)\ \mathrm{kJ \cdot mol^{-1}}$, and $\Delta_{sol}H_m\,(\mathrm{CuTPP}) = (15.6 \pm 0.1)\ \mathrm{kJ \cdot mol^{-1}}$. The enthalpies of solvation for the five compounds were also determined using the previously published values for the enthalpy of sublimation, as well as complementary data from the literature. The values obtained are as follows: $\Delta_{solv}H_m(\mathrm{TPP}) = -(158.3 \pm 2.1)\ \mathrm{kJ \cdot mol^{-1}}$, $\Delta_{solv}H_m(\mathrm{CoTPP}) = -(154.1 \pm 2.0)\ \mathrm{kJ \cdot mol^{-1}}$, $\Delta_{solv}H_m(\mathrm{CuTPP}) = -(149.4 \pm 5.0)\ \mathrm{kJ \cdot mol^{-1}}$ $\Delta_{solv}H_m(\mathrm{NiTPP}) = -(141.4 \pm 4.0)\ \mathrm{kJ \cdot mol^{-1}}$, and $\Delta_{solv}H_m(\mathrm{ZnTPP}) = -(140.5 \pm 3.0)\ \mathrm{kJ \cdot mol^{-1}}$. The results are analyzed in relation to several molecular properties such as ionic radius, electronic spectra, and Connolly surface. An explanation of the observed trends for solvation enthalpies is proposed.

Introduction

Porphyrins can be described as macrocyclic compounds formed from the chemical fusion of four pyrrole rings. This macrocycle, whose molecular structure is shown in Figure 1, is known as porphine and is not so stable. In contrast, its derivative obtained by substitution with phenyl groups in the meso-positions, known as tetra phenyl porphyrin (TPP), is included in a wide family of synthetic and natural molecules that are very stable. The complexation of metal ions by TPP leads to a formidable diversity of chemical compounds (MTPP) that in most of the cases studied is related to mimic the role of porphyrins in such essential processes as respiration or photosynthesis.[1] Probably TPP and MTPP (with M: Co(II), Ni(II), Cu(II), and Zn(II)) have been the more studied macrocycles as chemical or theoretical models to enlarge knowledge about the essential role of the porphyrins in nature. Also, porhyrins have many technological applications, going from photodynamic therapy[2−7] to molecular electronics and photonic devices[8−11] or their use as dyes in solar cells to improve efficiency.[12−15]

Through weak interactions in solution of an appropriate solvent, porphyrins exhibit interesting features of orientation between the molecules themselves, even at low

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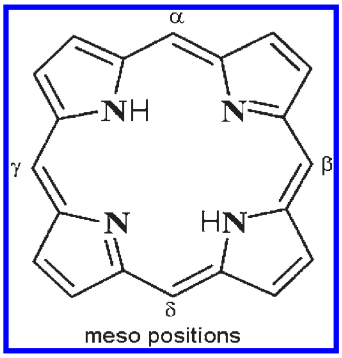

Figure 1. Porphine skeleton showing meso-positions.

concentrations these compounds are at the beginning of supramolecular aggregates,[16-21] a field in which it is really important to control the organization of entities by non covalent interactions[22,23] that are strongly dependent on the crystallization environment or solvation features. In this context, the determination of enthalpies of solvation through calorimetric measurements contributes to the comprehension of these phenomena. The porphyrins have been widely studied both chemically and spectroscopically,[24-32] but despite of their chemical, biological, and technological importance, there are very few thermodynamic studies of these compounds, particularly in solution. To our knowledge, apart of some enthalpies of formation in the solid and gaseous phases and derived bond energies published before,[33] there exists just one study determining the enthalpy of solution of some of these compounds,[34,35] but with scarce experimental details and condition that could permit a good assessment of the given results. In some cases different results from the same authors[36] are given from one year to another. In the absence of systematic studies of the solvation of these kinds of compounds from experimental measurements of the required thermodynamic properties, we have decided to start a calorimetric study of these compounds to know and understand the solvation behavior of large size, planar molecules in a polar solvent and contribute through experimental or theoretical studies to the developing knowledge of them.

Table 1. Maxima of the Absorption Bands in the Electronic Spectra (in nm) for the Studied Compounds[a]

		Q bands			
porphyrin	Soret	IV	III	II	I
TPP[39]	418 (417)	515 (514)	550 (550)	589 (593)	645 (646)
CoTPP[40]	410 (412)	528 (*528*)			
NiTPP[41]	415 (414)	528 (527)			
CuTPP[39]	415 (415)	539 (542)			
ZnTPP[41]	424 (425)	557 (559)		596 (599)	

[a] Figures in parentheses are from the literature.

Experimental Section

Preparation and Purification of Samples. All the solvents (methanol, benzene, and chloroform) and other compounds used during purification of samples and calorimetric experiments were obtained from Aldrich Chemical Co. and were purified by the recommended methods (Perrin et al.).[37] The free porphyrin and the metallic porphyrins were obtained from the same supplier. The 5,10,15,20-tetraphenylporphine (TPP) contains chlorin as an impurity. This was removed by refluxing a sample of 6 g from the flask, in 750 cm^3 of chloroform containing 1.5 g of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and 45 cm^3 of dried benzene, for at least 2 h, followed by elution through an alumina (Brockman I, standard grade from Sigma-Aldrich) column (30 × 2.5 cm), using freshly distilled chloroform.[38] Since the electronic spectra for the metalloporphyrins of Co(II), Ni(II), Cu(II), and Zn(II) revealed incomplete metalation of this compounds, an additional treatment was necessary. They were treated by reflux in chloroform containing an excess of the corresponding metallic acetate, for 1 to 5 h, depending on the metallic ion. ^{1}H NMR spectra were taken to verify the purity, and no traces of chlorin were detected (chemical shift at 4.15 ppm disappears). Complete metalation of TPP for the four studied ions was considered as successful when the number of the absorption bands of metalloporphyrins in relation to the number in TPP was reduced as described in the Table 1. Also, when the metalation occurs completely the band at 645 nm disappears. Guided by the thermogravimetric analysis, the samples of the crystallized porphyrin and metalloporphyrins were dried in a vacuum oven at 533 K.

Samples of the purified and dried compounds were placed in glass ampules for the calorimetric experiments. These ampules were weighed empty, containing the solute sample, and after sealing with a special burner, to determine the corresponding mass.

Because of the spontaneous decomposition of chloroform and the consequent increase of its acidity, that affects the calorimetric measurements, special care was taken to purify this solvent. It was purified by washing with water to remove ethanol, followed by drying with K_2CO_3 and later refluxed with $CaSO_4$ for 2 h and then distilled. Quantities of the solvent were prepared just for the calorimetric measurements of the same day

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and stored, if necessary, in the dark to avoid photochemical decomposition. Using precision pipettes of 100 and 25 cm^3, the freshly purified chloroform was introduced in the calorimetric cell and immediately closed with the stirrer assembly to avoid evaporation. The mass of the solvent to calculate molality was determined using the value of 1.478 g·cm^{-3} for the density of chloroform.

Calorimetric Measurements. The enthalpies of solution were determined from calorimetric experiments performed in a 2225 Precision Solution Calorimeter (Thermometric, Sweden), mounted in a Thermal Activity Monitor TAM III, provided with an ampule break system, stirrer holding glass ampules to contain solute samples, electrical calibration, data acquisition and analysis units, and software for automatic operation. The thermostatic bath was fixed at (298.15 ± 0.20) K and all the measurements were made at this temperature. Glass reaction vessels of 100 and 25 cm^3 were used to check complete and consistent solubility of the samples. Electrical calibrations, before and after the main calorimetric period for each experiment, were performed to determine the heat of solution, in such a way that the corrected temperature change during calibration would reproduce the corresponding one for the solution process. On the basis of the Regnault−Pfaundler method, the corrected temperature change was automatically calculated by the control and analysis system of the instrument. With the calibration results for each experiment, the involved energy quantity during dissolution of porphyrin in chloroform were determined using the corresponding corrected temperature change. Corrections for ampule breaking and evaporation were performed from blank calorimetric experiments breaking empty ampules. The corrections were dependent on the reaction vessel volume. The stirrer was set at 500 rpm, and the breaking of the ampule was made as close as possible to 60 mK below the bath temperature, and when the standard deviation of the fit, calculated over the last 5 min of the initial period, was better than 10 μK. Under these conditions, the calorimeter works in the high resolution range.

After each calorimetric measurement, an aliquot of solution was taken, and the electronic spectrum was immediately obtained. A few experiments were discarded when the spectra revealed shifts to greater wavelengths indicating aggregate formation. The intensity of signals was proportional to the porphyrin mass in each ampule. This verified the complete solution of samples.

The calorimetric reactions that occurs in the calorimeter and to which the enthalpy values are associated, for TPP and the corresponding metallic derivatives, can be represented as

$$\mathrm{TPP}_{(s)} + n\mathrm{CHCl}_{3(l)} = \mathrm{TPP}\cdot n\mathrm{CHCl}_3$$

and

$$\mathrm{MTPP}_{(s)} + n\mathrm{CHCl}_{3(l)} = \mathrm{MTPP}\cdot n\mathrm{CHCl}_3;$$

$$(\text{with M}: \mathrm{Co(II)}, \mathrm{Ni(II)}, \mathrm{Cu(II)}, \text{ and } \mathrm{Zn(II)})$$

Results

All the experimental data and results for the calorimetric measurements of the molar enthalpy of solution, $\Delta_{\mathrm{sol}}H_m$, for TPP, CoTPP, NiTPP, CuTPP, and ZnTPP are presented in Tables 2−6.

Table 2. Experimental Results for the Molar Enthalpy of Solution, $\Delta_{\mathrm{sol}}H_m$, of TPP, in Chloroform at 298.15 K

mass × 10^3 (g)	$n \times 10^6$ (mol)	$m \times 10^4$ (mol·kg^{-1})	$Q \times 10^3$ (J)	$\Delta_{\mathrm{sol}}H_m$ (kJ·mol^{-1})
0.80	1.30	0.35	34.0	26.2
0.84	1.37	0.37	33.8	24.7
1.13	1.84	0.50	48.5	26.4
1.80	2.93	0.79	66.1	22.6
3.70	6.02	1.63	129.7	21.6
4.40	7.16	1.94	162.4	22.7
4.71	7.66	2.07	166.7	21.8
4.87	7.92	2.14	167.1	21.1
5.16	8.39	2.27	161.9	19.3
5.22	8.49	2.30	182.0	21.4
10.03	16.32	1.10	371.0	22.7
12.25	19.93	1.35	423.1	21.2
14.80	24.08	1.63	518.1	21.5
19.95	32.45	2.20	665.7	20.5
24.23	39.42	2.67	809.1	20.5
24.85	40.42	2.74	831.7	20.6

Table 3. Experimental Results for the Molar Enthalpy of Solution, $\Delta_{\mathrm{sol}}H_m$, of CoTPP, in Chloroform at 298.15 K

mass × 10^3 (g)	$n \times 10^6$ (mol)	$m \times 10^4$ (mol·kg^{-1})	$Q \times 10^3$ (J)	$\Delta_{\mathrm{sol}}H_m$ (kJ·mol^{-1})
1.68	2.50	0.68	93.9	37.5
3.89	5.79	1.57	221.6	38.3
5.41	8.05	2.18	311.8	38.7
5.47	8.14	2.20	316.9	38.9
5.53	8.23	2.23	322.7	39.2
6.52	9.71	2.63	379.2	39.1
6.89	10.26	2.78	406.3	39.6

Table 4. Experimental Results for the Molar Enthalpy of Solution, $\Delta_{\mathrm{sol}}H_m$, of NiTPP, in Chloroform at 298.15 K

mass × 10^3 (g)	$n \times 10^6$ (mol)	$m \times 10^4$ (mol·kg^{-1})	$Q \times 10^3$ (J)	$\Delta_{\mathrm{sol}}H_m$ (kJ·mol^{-1})
5.74	8.55	0.58	130.4	15.2
5.83	8.68	0.59	132.6	15.3
8.48	12.63	0.85	194.7	15.4
10.97	16.34	1.11	245.7	15.0
11.37	16.93	1.15	257.1	15.2
12.82	19.09	1.29	284.7	14.9
13.11	19.53	1.32	295.2	15.1
18.42	27.43	1.86	400.4	14.6
18.45	27.48	1.86	409.3	14.9

Table 5. Experimental Results for the Molar Enthalpy of Solution, $\Delta_{\mathrm{sol}}H_m$, of CuTPP, in Chloroform at 298.15 K

mass × 10^3 (g)	$n \times 10^6$ (mol)	$m \times 10^4$ (mol·kg^{-1})	$Q \times 10^3$ (J)	$\Delta_{\mathrm{sol}}H_m$ (kJ·mol^{-1})
5.04	7.45	2.02	110.9	14.9
5.36	7.93	2.15	118.2	14.9
10.16	15.02	1.02	228.9	15.2
11.45	16.93	1.15	259.0	15.3
13.17	19.47	1.32	297.4	15.3
13.94	20.61	1.39	313.5	15.2
14.23	21.04	1.42	316.3	15.0
19.04	28.15	1.90	423.8	15.0

Through the linear fitting of the values for the molar enthalpy of solution as a function of the concentration, the values for the molar enthalpy of solution at infinite dilution were calculated for the free porphyrin and its metallic derivatives. The results of these calculations are summarized in Table 7. The uncertainty in this case represents the standard deviation of the fitting. Then, with the values of the molar enthalpy of solution at infinite dilution and the

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Table 6. Experimental Results for the Molar Enthalpy of Solution, $\Delta_{sol}H_m$, of ZnTPP in Chloroform at 298.15 K

mass × 10^3 (g)	$n \times 10^6$ (mol)	$m \times 10^4$ (mol·kg^{-1})	$Q \times 10^3$ (J)	$\Delta_{sol}H_m$ (kJ·mol^{-1})
2.22	3.27	0.89	177.7	54.3
2.73	4.03	1.09	218.2	54.2
4.42	6.52	1.76	347.1	53.2
5.03	7.42	2.01	391.0	52.7
5.30	7.82	2.12	412.9	52.8
5.48	8.08	2.19	425.3	52.6
5.63	8.30	2.25	435.7	52.5
5.80	8.55	2.31	450.6	52.7
5.87	8.66	2.34	453.3	52.4

Table 7. Molar Enthalpies of Solution at Infinite Dilution, Sublimation, and Solvation, at 298.15 K

porphyrin	$\Delta_{sol}H_m$ kJ·mol^{-1}	$\Delta_{sub}H_m$ kJ·mol^{-1}	$\Delta_{solv}H_m$ kJ·mol^{-1}	ref.
TPP	25.7 ± 0.6	184 ± 2.0	−158.3 ± 2.1	42
CoTPP	36.9 ± 0.2	191 ± 2.0	−154.1 ± 2.0	42
NiTPP	15.6 ± 0.1	157 ± 4.0	−141.4 ± 4.0	43
CuTPP	15.6 ± 0.1	165 ± 5.0	−149.6 ± 5.0	43
ZnTPP	55.6 ± 0.2	196 ± 3.0	−140.5 ± 3.0	42

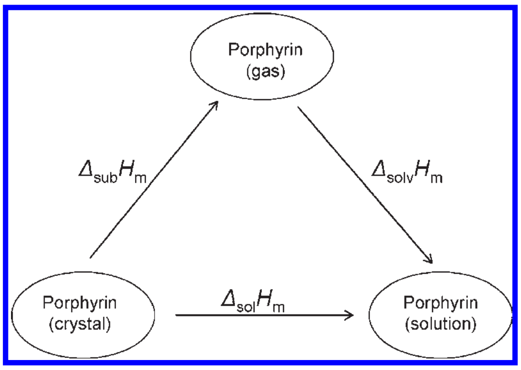

Figure 2. Thermodynamic cycle representing the experimental approach to determine the enthalpy of solvation.

corresponding values for the molar enthalpy of sublimation, determined previously in this laboratory[42] for TPP, Co(II)TPP, and Zn(II)TPP, and from the literature values[43] for Ni(II)TPP and Cu(II)TPP, the molar enthalpies of solvation were obtained as $\Delta_{solv}H_m = \Delta_{sol}H_m - \Delta_{sub}H_m$. The experimental approach to determine the enthalpy of solvation is represented in the thermodynamic cycle of Figure 2:

The results of this calculation are also included in Table 7. The uncertainty in the enthalpy of solvation takes into account the uncertainty on the individual values for the molar enthalpies of solution and sublimation.

The results for the molar enthalpies of solution and sublimation follow the same trend $\Delta_{sol}H_m$/(kJ·mol^{-1}): NiTPP(15.6 ± 0.1), CuTPP(15.6 ± 0.1), TPP (25.7 ± 0.6), CoTPP (36.9 ± 0.2), ZnTPP (55.5 ± 0.2), and $\Delta_{sub}H_m$/(kJ·mol^{-1}): NiTPP(157 ± 4.0), CuTPP(165 ± 5.0), TPP (184 ± 2.0), CoTPP (191 ± 2.0), ZnTPP (196 ± 3.0). This is consistent with the associated processes, since both solution and sublimation processes require the breaking of bonds in the crystal lattice and expansion of molecules into the solvent or into the vacuum, respectively. Thus, the enthalpies of solvation determined from these experimental values can be considered as reliable.

Discussion

The dissolution of the solid porphyrin and metalloporphyrins in liquid chloroform, studied in this work, are endothermic processes in all cases. That means that the interaction energy of the porphyrin molecules with the *n*-molecules of solvent is higher than the sum of solid−solid interaction energy of the porphyrin molecules in the solid phase and the liquid−liquid interaction energy between the chloroform molecules. The solution process of the solid porphyrins involves an energy transfer from the solvent that during the experiments occurs under quasi-adiabatic conditions; this transfer creates order in the structure of the solution. This must be understood as a decrease of the number of microstates considered in a statistical thermodynamics approach. In other words, because the porphyrin and the chloroform molecules assume certain preferred orientations, some degrees of freedom of the molecules of chloroform and the porphyrin itself are lost as the solution process occurs. An equivalent argument for exothermic processes increasing the entropy and disorganization of the system has been proposed by Airoldi and co-workers.[44] In the case of TPP that behaves as an ampholite, the preferred orientations generating structure are related to the possible types of interaction with the chloroform molecules. Some evident interactions take place through two acidic nitrogen atoms, two nitrogen atoms of basic character, and through the conjugated system of π electrons. In contrast, the metalloporphyrins must interact with the solvent molecules in a different way, because the acidic nitrogen atoms are not present, the four basic nitrogen atoms of the macrocycle are mainly involved in the coordination bond with the metallic ion and just the conjugated system of π electrons remains for interaction with solvent molecules. The metallic ion appears to play an important role as a center for interaction with chloroform molecules during solvation. The electronic spectra in chloroform of TPP and the studied metalloporphyrins provide additional evidence that the porphyrin molecules induce order in the structure in the bulk of the chloroform solution. The disappearance of some of the absorption bands for the metalloporphyrins in their electronic spectra is indicative of a more symmetrical system[45] and the consequent decrease of the microscopic states related to the electronic transitions. Also, keeping in mind that the chloroform molecules are really small compared to the porphyrin size, the actual number of molecules in the solvation shell is much more than just the number of those that can interact directly through the above-described preferred orientations. This could be supported by the very large absolute values for the enthalpy of solvation.

As shown in Table 7 and Figure 3, the enthalpies of solution for the studied metalloporphyrins are clearly dependent on the ionic radius of the involved metal. The solution

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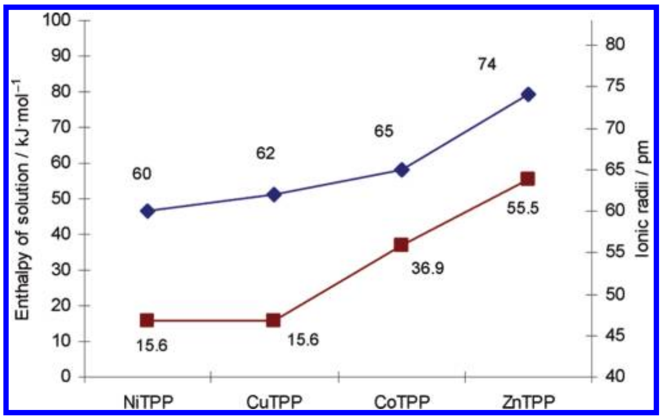

Figure 3. Enthalpy of solvation and ionic radii showing the same trend.

process of the metalloporphyrins in chloroform is more endothermic when the ionic radius increases. The Zn(II) has the biggest ionic radius, and the more endothermic enthalpy of solution would generate a major structure in the bulk of solution. In the case of the NiTPP and CuTPP, that have practically the same ionic radii[46] (60 and 62 pm, respectively), our results for the enthalpy of solution were the same (15.6 kJ·mol^{-1}). Even if such a precise coincidence does not occur with the CoTPP and ZnTPP that have ionic radii[46,47] of 65 and 74 pm, respectively, the influence of the ionic radius is observed.

The solvation of TPP and its derivatives in chloroform is understood as a process in which a molecule of the compound, in the gas phase, that behaves as an independent molecule, is introduced in an excess of solvent to ensure that the solute molecules can be considered as non interacting particles between themselves. By this reason, the molar enthalpies of solvation for each compound were determined with the corresponding enthalpies of solution at infinite dilution and with the enthalpies of sublimation that can only be experimentally determined under reduced pressure.

The solvation process can be visualized in at least four steps:[48] (a) the cavitation in the bulk of solvent, leaving the space to receive a solute molecule, (b) the rearrangement of the solvent molecules perturbed by the presence of solute molecules, (c) the arrangement between solute and solvent molecules through anisotropic weak and specific interactions solute−solvent, like those already described above, and (d) the total covering of solute molecule by the solvent, through isotropic interactions achieving the closure of the cavity in which the solute molecule is completely surrounded by solvent molecules as close as permitted by the chemical nature of solute and solvent. In this context, the solvation enthalpy depends on the number and energy of solute−solvent interactions and also, for larger size molecules, on the available surface to be covered by solvent molecules. The solvation enthalpy values in the condensed phase, can be considered as the sum of energies associated to the above-described steps. The desolvation process can be visualized as the aperture of cavity, followed by breaking of isotropic and anisotropic or specific interaction, and finally the escape of solute molecule to the gas phase. From our experimental results the molar desolvation enthalpy is endothermic for TPP and its Co, Cu, Ni, and Zn derivatives.

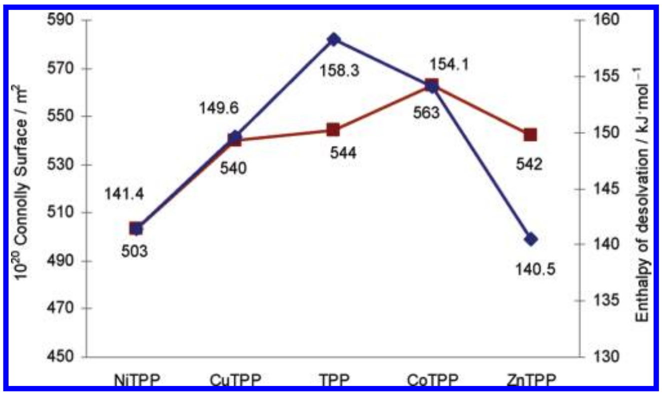

Figure 4. Trend of enthalpy of desolvation and Connolly surface.

All the solvation processes for the studied compounds are exothermic, and the trend for exothermicity is TPP > CoTPP > CuTPP > NiTPP > ZnTPP. From these results, it is clear that TPP accepts the biggest number of chloroform molecules because of the really large difference in size and diversity of possible types of interaction between $CHCl_3$ and TPP molecules. Because TPP has the more important enthalpy of solvation, it is evident that the energy of interaction between the metallic ion of metalloporphyrins and $CHCl_3$ does not compensate for the energy of interaction of the acidic and basic nitrogen atoms in free TPP with the chloroform molecules.

To explore if effectively the molar enthalpy of solvation is correlated with the available surface to be covered by $CHCl_3$ molecules and if the specific interactions could also be detected from the enthalpy of solvation values, the corresponding Connolly surface was determined for each of the porphyrins studied in this work.

The van der Waals surface that is accessible to a solvent molecule having a nonzero radius is known as the Connolly surface,[49] and was determined from the Cambridge Structural database[50] using the software Materials Studio,[51] for each studied compound. The Connolly surface is taken in this study as indicative of the number of solvent molecules that are not interacting in a specific way but considered as a cumulative interaction of all the chloroform molecules covering the available surface of the porphyrin molecules.

The Connolly Surface (CS) values, expressed as $(10^{20}\cdot CS)/m^2$, are shown in parentheses for each compound as follow: NiTPP (503.2), CuTPP (540.3), ZnTPP (542.1), TPP (543.7), and CoTPP (563.4).

In Figure 4, the enthalpy of desolvation and the Connolly surface are displayed to show the trend of the two properties; even the corresponding points are practically superposed for NiTPP, CuTPP, and CoTPP. The deviation of the enthalpy of desolvation for the TPP and ZnTPP from the value expected just from the isotropic interaction involved in the covering of the solute molecule surface by the solvent is only apparent. The anisotropic interactions of acidic and basic nitrogen atoms of TPP with the solvent, that are not present

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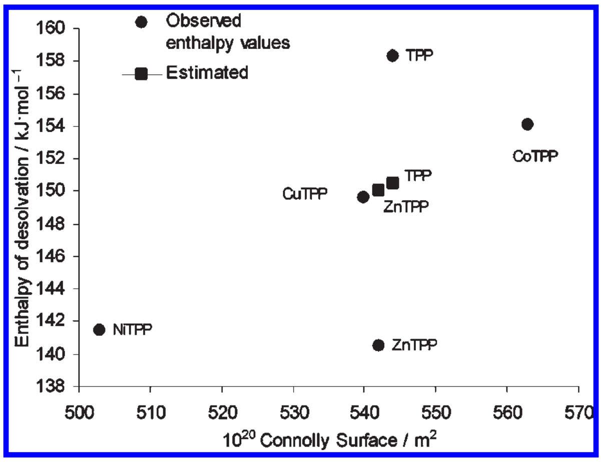

Figure 5. Linear estimation of the enthalpy of solvation values (■) for TPP and ZnTPP, considering just anisotropic interactions of them, with solvent molecules.

in the metalloporphyrins, are responsible for a more endothermic enthalpy of desolvation (or a more exothermic enthalpy of solvation). The specific contribution of the four $N-CHCl_3$ interactions to the enthalpy of desolvation from this correlation can be estimated as 8 $kJ\cdot mol^{-1}$. The enthalpy of desolvation of ZnTPP is less endothermic than expected for around 10 $kJ\cdot mol^{-1}$. This can be attributed to the lower coordination numbers normally shown by Zn in comparison with the other ions and could be explained by remembering that the biggest atomic radius of Zn(II) permits the coordination of one $CHCl_3$ molecule as the "fifth ligand", while smaller ionic radii of Ni(II), Cu(II), and Co(II) permit a second molecule of $CHCl_3$ as the "sixth ligand". Thus, the lower enthalpy of desolvation from the expected value is consistent with this coordination feature. The estimated values for the specific interaction were obtained from an expected linear dependence between the enthalpy of desolvation and the Connolly surface, considering just the anisotropic interactions. In Figure 5 are displayed the experimentally measured and estimated values for the enthalpy of desolvation. The values of 8 and -10 $kJ\cdot mol^{-1}$, for the specific contribution to the enthalpy of desolvation of the four $N-CHCl_3$ interactions and for the absence of second molecule of $CHCl_3$ as the "sixth ligand" in the case of ZnTPP, were estimated as the difference between measured and estimated corresponding values.

Acknowledgment. This research is partially fulfilled by CONACYT (Mexico) (Project C01-41872) and the scholarship of M.G. The authors acknowledge Drs. M. J. Rosales, A. Paz, and J. Tiburcio for helpful revision of the manuscript.