Inorg. Chem. 2007, 46, 9332–9336

Inorganic Chemistry

Article

Strength of the Zn–N Coordination Bond in Zinc Porphyrins on the Basis of Experimental Thermochemistry

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Received February 8, 2007

The compound, 5,10,15,20-tetrakis(4-methoxyphenyl)porphine zinc(II) (ZnTMPP), was prepared, and its thermochemical properties were experimentally established. The standard molar energy of combustion ($\Delta_c U^\circ_m$) was determined from oxygen rotating-bomb combustion calorimetry experiments. The standard molar enthalpies of combustion ($\Delta_c H^\circ_m$) and formation ($\Delta_f H^\circ_m$) were derived. The enthalpy of sublimation ($\Delta_{cr}{}^{g}H^\circ_m$) was determined by Knudsen effusion at high temperatures. With these results, the standard molar enthalpies of formation and atomization ($\Delta_{at}H^\circ_m$) in the gas state were calculated. A summary of the results at $T = 298.15$ K ($p^\circ = 0.1$ MPa) is shown in Table 1. Using these results and those previously obtained for the free ligand, 5,10,15,20-tetrakis(4-methoxyphenyl)porphine, the mean dissociation enthalpy for the Zn–N coordination bond is obtained as D(Zn–N) $= (160 \pm 9)$ kJ·mol^{-1}. This value is consistent with the results obtained using the same experimental approach in a similar system (5,10,15,20-tetraphenylporphine, TPP/ZnTPP) reported elsewhere. A discussion of the strength for the Zn–N coordination bond is made in terms of the structural and electronic features of the molecules involved.

Introduction

From an energetic point of view, chemical bonding has been approached using experimental (thermochemical) and theoretical methods.At present, knowledge of the energy for typical bonds involved in organic molecules is known, or estimations with a high reliability are possible. In contrast, not much research in molecular thermochemistry of coordination or organometallic compounds has been performed because of the very specialized techniques and procedures required.[1]

Large molecules of biological interest like cobalamins have been studied by kinetics of thermolysis[2,3] or iodination.[4] Both of these kinds of studies led to the indirect determination of mean bond dissociation enthalpies of Co−C in solution. A density functional theory study of Co−C bond dissociation energy in cobalamins[5] has produced correlations between optimized bond lengths and bond energies calculated from total energies of gaseous and isolated molecules. However, assessment of these results is not possible because the corresponding experimental data are available only in solution. An ab initio study[6] on free porphine and first row transition-metal porphyrins leading to an indication of the metal−nitrogen strength has been reported.

Table 1

ZnTMPP	(kJ·mol^{-1})
$\Delta_c U^\circ_m$ (cr)	-24235 ± 14
$\Delta_c H^\circ_m$ (cr)	-24249 ± 14
$\Delta_f H^\circ_m$ (cr)	-135 ± 16
$\Delta_{cr}{}^{g}H^\circ_m$	238 ± 4
$\Delta_f H^\circ_m$ (g)	103 ± 16
$\Delta_{at} H^\circ_m$ (g)	45163 ± 27

The importance of free and metallic synthesized porphyrins has been described already,[7] and the synthesis of new zinc

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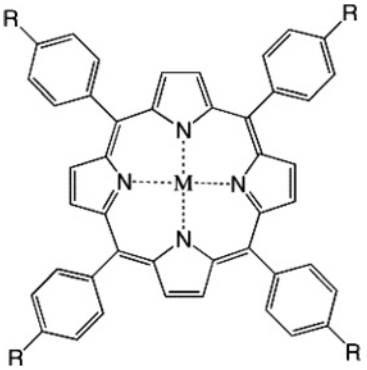

Figure 1. The general structure of the ZnTMPP (R = -OCH_3, M = Zn) reported here and those porphyrins cited previously: ZnTPP[7] (R = -H, M = Zn), TMPP[15,16] (R = -OCH_3, M = 2H), and TPP[15,16] (R = -H, X = 2H).

porphyrins is today a challenge as a consequence of their enormous applications.[8] Despite its importance in chemical and biological processes,[9] the nature of the Zn−N interaction is poorly understood. Some efforts have been made from spectroscopic[10] and analytical[11] points of view. The reports from Chagas and Airoldi[12−14] have provided approximate values for the mean dissociation enthalpy of the Zn−N bond in some coordination compounds. These values were derived from experimental enthalpies of formation in solution and estimation of the corresponding enthalpies of sublimation. The first mean bond dissociation enthalpy D(Zn−N), determined from the experimental enthalpy of formation in the gas phase for such a large and complex molecule like the zinc(II) 5,10,15,20-tetraphenylporphine (ZnTPP) has recently been reported.[7]

The simplest synthesized porphyrins, like those studied in the present and previous work,[7,15,16] constitute excellent models to obtain mean dissociation enthalpies when the porphyrins are coordinated to the Zn(II) ion. The aim of this work is to determine the mean bond dissociation enthalpy D(Zn−N) involved in 5,10,15,20-tetrakis(4-methoxyphenyl)-porphine (ZnTMPP, see Figure 1) from combustion and sublimation experiments of this compound. This will allow us to assess the accuracy and sensitivity of the experimental approach to observe the effect of four methoxy substituent groups on D(Zn−N), in relation to the compound studied previously.[7] The results could be used as reference for theoretical approaches of Zn−N bonding. Differences and similarities between both ZnTPP and ZnTMPP have been found in spectroscopic,[17,18] electrochemical,[18,19] and theoretical[20] studies.

Experimental Section

Preparation and Purification of the Sample. ZnTMPP is not commercially available and was prepared from 5,10,15,20-tetrakis-(4-methoxypenyl)-21H, 23H-porphine (TMPP, Aldrich Chemical Co.). As provided, the sample of TMPP was contaminated with the corresponding chlorin (a 7,8-dihydroporphyrin). Sample purification was achieved, and proved by ^{1}H NMR, as previously described.[15,21,22] The chlorin-free TMPP was dissolved in boiling chloroform and refluxed with a saturated solution of zinc acetate in methanol, as described by Abraham et al.[23] After evaporation of the solvent to almost dryness, cold methanol was added. Filtration afforded the pure ZnTMPP as a purple powder, that was dried overnight at $T = 360$ K in a vacuum oven.

There is a characteristic band for free TMPP ($\lambda = 650$ nm) but not for ZnTMPP when the visible-absorption spectrophotometric analysis of the sample is performed. It permits the detection of small amounts of free TMPP in the sample, and the coordination reaction must be repeated with zinc acetate when necessary.

Purity of the final sample of ZnTMPP was confirmed by ^{1}H NMR visible-absorption spectrophotometry and differential scanning calorimetry (DSC). DSC experiments under a nitrogen atmosphere revealed an endothermic process at temperatures around $T = 393$ K when ZnTMPP is aged some days in a vial at normal atmosphere conditions or several hours when the sample is introduced in a vessel with the same conditions of oxygen and humidity as in the bomb combustions. When the sample is reheated, the endothermic process does not occur. This could be interpreted as an axial coordination of a molecule of water to Zn(II) in ZnTMPP, since there are numerous examples of axial coordinated ligands to the planar square structure of metal porphyrins; nevertheless, further work should be done to confirm the coordination proposed here. Anyway, the sample was stored in a vacuum oven at $T = 423$ K before every combustion experiment. Moreover, a reversible process was found by DSC for the purified sample at temperatures around $T = 320$ K, involving a very small energy change. Finally, decomposition of the ZnTMPP occurs during melting at $T = 770$ K, and DSC was not suitable as a technique for purity determination of the sample by the melting method.

Combustion Calorimetry Experiments. The combustion experiments of a zinc-porphyrin have been detailed elsewhere.[7] Benzoic acid (SRM 39j) was used as a combustion calorimetric standard, and auxiliary material was supplied by NIST. Oxygen ($x = 0.9999$) was obtained from Alphagaz (U.S.A.). A rotating-bomb calorimeter (Argonne National Laboratory design) was used with the combustions bomb (Parr Instrument Co., 1004C). The experiments were performed in the presence of oxygen at $p = 3.0$ MPa and of a volume of 10 cm^3 of a HNO_3 (aq) dissolution ($c = 2.0$

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Table 2. Physical Properties at $T = 298.15$ K[c]

substance	composition	M^a ($g{\cdot}mol^{-1}$)	ρ ($g{\cdot}cm^{-1}$)	$(\delta u/\delta p)T$ ($J{\cdot}g^{-1}{\cdot}MPa^{-1}$)	c_p ($J{\cdot}K^{-1}{\cdot}g^{-1}$)
ZnTMPP	$C_{44}H_{28}N_4O_4Zn$	798.2	(1.275)	(−0.1)	1.353[b]
benzoic acid	$C_7H_6O_2$	122.121	1.320[27]	−0.115[27]	1.21[27]
cotton	$CH_{1.774}O_{0.887}$	27.9903	1.5[27]	−0.289[27]	1.7[27]

[a] Molar masses are based on the 2005 IUPAC recommendation.[26] [b] Heat capacity determined by DSC in this work. [c] M is the molar mass of the sample; ρ is the density; $(\delta u/\delta p)_T$ is the isothermal variation of the massic energy with pressure; and c_p is the massic heat capacity (estimated values are in parentheses).

$mol{\cdot}dm^{-3}$). Two hundred seconds after ignition, the combustion bomb was rotated until the end of each experiment.

During experiments, the temperature of the calorimetric vessel (with 2708 g of distilled water) was measured every 10 s with a linearized thermistor connected to a multimeter (Keithley, 2001). The energy equivalent of the calorimeter has been previously determined as ϵ(calor) = (14039.1 ± 0.4) $J{\cdot}K^{-1}$; the quoted uncertainty represents the standard deviation of the mean. From 12 comparison experiments combusting benzoic acid in the presence of ZnO, a different value for the energy equivalent was obtained: ϵ_{comp}(calor) = (14044.9 ± 3.2) $J{\cdot}K^{-1}$. This value includes the energetic processes after the combustion reaction to obtain, as closely as possible, the same final state as in the porphyrin combustion experiments.

The energy of combustion of purified ZnTMPP was determined from ten independent experiments. To ensure complete combustion, a pellet of benzoic acid was required as an auxiliary material. Corrections to standard states for the experimental reaction were computed according to the usual procedures.[24,25] The physical properties summarized in Table 2 were used to transform apparent mass to mass and for the calculations of the standard massic energy of combustion. The energy of combustion of the ZnTMPP was determined for aged samples, showing differences with fresh samples with values as low as $\Delta_c u° = -29415$ $J{\cdot}g^{-1}$ when compared to the mean value $\Delta_c u° = (-30361.8 \pm 18.0)$ $J{\cdot}g^{-1}$ (Table 5). To diminish the possible effects of aging, all the experiments were carried out with ignition 1 h after oxygen addition. Nevertheless, the significant deviation of the experimental values of energy of combustion could not be diminished.

Sublimation Experiments. The enthalpy of sublimation was determined by the Knudsen effusion method. The experimental procedure and the data analysis have been detailed elsewhere.[16] A special system with metal-glass joints was constructed to work at temperatures up to $T = 593$ K. The effusion orifice diameter was 2.3 mm. Samples of around 20 mg were placed into the effusion cell and heated near 600 K with an electric resistance. The system was under vacuum with a turbo molecular pump. The amount of sublimed ZnTMPP was detected with a piezoelectric quartz crystal under a cold finger with liquid nitrogen. The thickness increment of the crystal was directly measured every 120 s. Four series of experiments were made between $T = 583$ K and $T = 593$ K. Experiments at lower temperatures were not sensitive enough. The rate of sample condensing (dL/dt) was determined at different temperatures using a least-squares fitting, and the values were considered proportional to the corresponding vapor pressure as presumed by the Knudsen equation. Then, it is possible to obtain an integrated Clausius-Clapeyron equation

Table 3. Summary of Ideal Reactions Occurring during Combustion Experiments[a,b]

combustion experiments

1. $10.9 \cdot (C_7H_6O_2 + 7.5O_2 = 7CO_2 + 3H_2O)$
2. $C_{48}H_{36}N_4O_4Zn + 55.5O_2 = 48CO_2 + 18H_2O + ZnO + 2N_2$
3. $ZnO + 45.2HNO_3 \bullet 1243.2H_2O = Zn(NO_3)_2 \bullet 43.2HNO_3 \bullet 1244.2H_2O$
4. $C_{48}H_{36}N_4O_4Zn + 10.9C_7H_6O_2 + 137.3O_2 + 45.2HNO_3 \bullet 1243.2H_2O = 124.3CO_2 + Zn(NO_3)_2 \bullet 43.2HNO_3 \bullet 1286.1H_2O + 2N_2$

[a] Reaction 4 is the addition of reactions 1, 2, and 3. [b] Symbol · refers to a multiplication; symbol • refers to a chemical association.

$$\ln \frac{dL}{dt} T^{1/2} = \ln B - \frac{\Delta_{sub}H}{RT}$$

where B is a constant value. Plotting $\ln[(dL/dt){\cdot}T^{1/2}]$ versus T^{-1}, a least-squares fitting led to the enthalpy of sublimation.

Results

In Table 3, the total idealized chemical process occurring during the combustion experiment is displayed. Combustion reactions of benzoic acid as an auxiliary material and of ZnTMPP are represented by eqs 1 and 2, respectively. The energy associated with the combustion of benzoic acid is precisely known. Equation 3 represents the dissolution of the zinc oxide formed during combustion in the nitric acid solution. The small energy involved by dissolution is considered in ϵ_{comp}(calor), in addition to other lateral physical processes such as heating, cooling, mixing, and gas dissolution. Every effort was made to obtain very similar final states in both comparison and combustion experiments. The total idealized chemical process is summarized in eq 4. The amounts of carbon dioxide, water, and zinc nitrate produced are closely the same as in comparison experiments. The mean value[7] of ϵ_{comp}(calor) = (14044.9 ± 3.2) $J{\cdot}K^{-1}$ was used to calculate the standard massic energy of combustion of ZnTMPP.

To follow the scheme of calculation, the typical masses and energies involved during combustion experiments are presented in Table 4. The value for entry (16) is just (15) divided by (1), the value for (15) is obtained by summing entries (9)+(10)+(11)+(12)+(13)+(14), and the value for entry (9) is just the experimental ΔT (8) multiplied by the calorimeter constant, ϵ(calor). From ten combustion experiments summarized in Table 5, the value $\Delta_c u°$(ZnTMPP, cr) = −(30361.8 ± 18.0) $J{\cdot}g^{-1}$ at $T = 298.15$ K was obtained. The uncertainty represents the standard deviation of the mean.

Four series of effusion experiments are summarized in Table 6. The variation of the thickness of the sublimed sample was detected by the piezoelectric crystal with time and computed at different temperatures. Variation of these values with temperature allows the calculation of the enthalpy of sublimation for each series. A mean value was obtained as $\Delta_{cr}{}^{g}H°_m$ (ZnTMPP) = (223.7 ± 4.4) $kJ{\cdot}mol^{-1}$ at the mean temperature $T = 588$ K. Correction of this value to $T =$

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Table 4. Typical Masses and Energy Quantities for the Combustion Experiments at $T = 298.15$ K[a]

	ZnTMPP
1) m'(ZnTPP)/g	0.303516
2) m''(benzoic acid)/g	0.499727
3) m'''(cotton)/g	0.002316
4) m(Pt)/g	12.804822
5) n_l(Zn)/mol	0.00038
6) $n_l(H_20)$/mol	0.52
7) $n_l(HN0_3)$/mol	0.02
8) $\Delta T/K = (t_l - t_f + \Delta T_{corr})$/K	−1.59613
9) ϵ(calor) (ΔT)/kJ	−22.4175
10) ϵ(cont)(ΔT)/kJ	−0.0812
11) $\Delta u_{dec}(HNO_3)$/KJ	0.0196
12) ΔU(corr. to std. states)/kJ	0.0335
13) $-m'''\cdot\Delta_c u°$(cotton)/kJ	0.0392
14) $-m''\cdot\Delta_c u°$(benzoic acid)/kJ	13.1996
15) $m'\cdot\Delta_c u°$(ZnTPP)/kJ	−9.2068
16) $\Delta_c u°$(ZnTPP)/(kJ·g^{-1})	−30.3338

[a] $p° = 0.1$ MPa. The quantities are reported according to the thermochemical protocol; m represents the mass of various samples, and n_l is used for the initial molar quantities of substances (before combustion), ΔT is the corrected temperature rise during the combustion process, ϵ(calor) is the heat capacity of the combustion bomb (also known as the calorimeter constant), ϵ(cont) is the heat capacity of the different substances inside the combustion bomb, ΔU(corr. to std. states) is the contribution to the internal energy change of the process when corrections to the standard states are applied, and $\Delta_c u°$ is the standard energy of combustion for every substance.

Table 5. Summary of the Standard Massic Energies of Combustion of ZnTMPP at $T = 298.15$ K[a]

	combustion experiments $\Delta_c u°$(ZnTMPP)/(J·g^{-1})
	−30307.8
	−30331.2
	−30292.2
	−30419.4
	−30333.8
	−30400.9
	−30433.5
	−30432.1
	−30372.2
	−30294.4
mean value	−30361.8
standard deviation of the mean	18.0

[a] $p° = 0.1$ MPa.

298.15 K requires knowledge of the heat capacity of the gaseous compound.

Experimental values of this heat capacity are not available, and estimation from group contributions is not possible with the available data. For this reason, the classical value proposed by Burkinshaw and Mortimer[28] $\Delta c_p = c_p(g) - c_p(cr) = -50$ J·mol^{-1}·K^{-1} for a number of different molecular structures, as suggested by Pedley in a personal communication, was applied. A correction of 14.5 kJ·mol^{-1} for the molar enthalpy of sublimation of ZnTMPP leads to a value of $\Delta_{cr}{}^{g}H°_m(298.15\ K) = (238.2 \pm 4.4)$ kJ·mol^{-1}. It is important to keep in mind that this is an approximate but necessary correction. However, since this same correction was made with the other three porphyrins in previous reports,[7,15,16] it is possible to compare without higher errors the corresponding values for the enthalpies of sublimation, of formation in gas phase, and of atomization.

Table 6. Experimental Values for Determination of the Molar Enthalpy of the Sublimation of ZnTMPP Using the Quartz-Crystal Microbalance[c]

T/K	$10^3\cdot(dL/dt)$/nm·s^{-1}	$10^2\cdot\Delta$	T/K	103·(dL/dt)/nm·s^{-1}	$10^2\cdot\Delta$
Series 1: $\Delta_{cr}{}^{g}H°_m = (217.7 \pm 4.1)$ kJ·mol^{-1} at $<T> = 588.2$ K[a]					
583.2	2.6163	0.33	589.2	4.1337	0.90
585.2	2.9815	−1.77	591.2	4.7164	−0.76
587.2	3.5659	1.45	593.2	5.4990	−0.16
Series 2: $\Delta_{cr}{}^{g}H°_m = (215.6 \pm 10.8)$ kJ·mol^{-1} at $<T> = 588.2$ K					
584.2	2.5255	−1.65	590.2	4.0696	1.44
586.2	3.0696	2.89	592.2	4.6018	−0.94
588.2	3.4019	−1.71			
Series 3: $\Delta_{cr}{}^{g}H°_m = (226.5 \pm 2.8)$ kJ·mol^{-1} at $<T> = 588.2$ K					
583.2	2.0296	−0.91	589.2	3.2695	−0.30
585.2	2.4267	1.16	591.2	3.8448	0.43
587.2	2.8068	0.02	593.2	4.4459	−0.42
Series 4: $\Delta_{cr}{}^{g}H°_m = (230.2 \pm 9.6)$ kJ·mol^{-1} at $<T> = 588.2$ K					
584.2	2.1094	0.72	590.2	3.3014	−2.13
586.2	2.4177	−1.63	592.2	3.9835	0.98
588.2	2.9425	2.13			
Mean Value: $\Delta_{cr}{}^{g}H°_m = (223.7 \pm 4.4)$ kJ·mol^{-1} at $<T> = 588.2$ K[b]					

[a] Uncertainty σ_i of individual values represents the standard deviation of the linear fitting. [b] The weighted average μ and the corresponding uncertainty σ_s were calculated from $\mu = \Sigma(x_l/\sigma_l^2)/\Sigma(\sigma_l^{-2})$ and $\sigma_s = [\Sigma(\sigma_l^{-2})]^{-1/2}\cdot N^{1/2}$ with N being the number of series. [c] L is the thickness of the sample deposited on the piezoelectric crystal, and Δ is the uncertainty from a least-squares fitting. Effusion-orifice diameter: 2.3 mm.

A reversible transformation in the solid phase was found for ZnTMPP by DSC experiments. When samples were heated, an endothermic process began at temperatures over $T = 313$ K with $\Delta H = (2.36 \pm 0.07)$ kJ·mol^{-1}. When cooling, an exothermic process began at temperatures below $T = 328$ K with $\Delta H = -(2.5 \pm 0.3)$ kJ·mol^{-1}. In all five heating/cooling experiments, the mass of the samples was conserved. The low energy involved in the process and the reversibility suggest a structural rearrangement.

The derived enthalpies of formation and atomization in gas phase of ZnTMPP at $T = 298.15$ K were calculated from the combustion and sublimation experimental results and using the following values:[29] $\Delta_f H_m°[CO_2(g)] = -(393.51 \pm 0.13)$ kJ·mol^{-1}, $\Delta_f H_m°[H_2O(l)] = -(285.83 \pm 0.04)$ kJ·mol^{-1}, $\Delta_f H_m°[ZnO(cr)] = -(350.46 \pm 0.27)$ kJ·mol^{-1}, $\Delta_f H_m°[C(g)] = (716.68 \pm 0.45)$ kJ·mol^{-1}, $\Delta_f H_m°[H(g)] = (217.998 \pm 0.006)$ kJ·mol^{-1}, $\Delta_f H_m°[N(g)] = (472.68 \pm 0.40)$ kJ·mol^{-1}, $\Delta_f H_m°[O(g)] = (249.18 \pm 0.10)$ kJ·mol^{-1}, and $\Delta_f H_m°[Zn(g)] = (130.40 \pm 0.40)$ kJ·mol^{-1}. Results are given in Table 7. Columns in the same table contain the corresponding quantities for the free ligands TMPP and TPP as well as for the ZnTPP, previously reported.[7,15,16]

Discussion

Previous reports for combustion and sublimation experiments of ZnTMPP are not known. Not even the elucidation of either the TMPP or ZnTMPP structures by X-ray diffraction analysis have been found in the literature. Comparison of their enthalpies of formation shows a stabilization of the zinc porphyrin in relation to the free TMPP, in the solid phase (204 kJ·mol^{-1}) as in the gas phase (192 kJ·mol^{-1}). However, this stabilization is around 100 kJ·mol^{-1} lower than in the pair TPP/ZnTPP.[7]

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Table 7. Standard Molar Thermochemical Functions for TMPP and ZnTMPP at $T = 298.15$ K[a]

	ZnTMPP	TMPP	ZnTPP[7]	TPP
$\Delta_cU^\circ_m$(cr)/kJ·mol^{-1}	−24235 ± 14	−24375 ± 7[15]	−22007 ± 7	−22244 ± 7[15]
$\Delta_cH^\circ_m$(cr)/kJ·mol^{-1}	−24249 ± 14	−24388 ± 7[15]	−22021 ± 7	−22257 ± 7[15]
$\Delta_fH^\circ_m$(cr)/kJ·mol^{-1}	−135 ± 16	69 ± 9[15]	354 ± 9	655 ± 9[15]
$\Delta_{cr}^{g}H^\circ_m$/kJ·mol^{-1}	238 ± 4	226 ± 10[16]	196 ± 3	184 ± 2[16]
$\Delta_fH^\circ_m$(g)/kJ·mol^{-1}	103 ± 16	295 ± 14[16]	550 ± 9	839 ± 9[16]
$\Delta_{at}H^\circ_m$(g)/kJ·mol^{-1}	45163 ± 27	45277 ± 25[16]	39109 ± 22	39125 ± 22[16]

[a] $p^\circ = 0.1$ MPa. $\Delta_cU^\circ_m$, $\Delta_cH^\circ_m$, $\Delta_fH^\circ_m$, $\Delta_{cr}^{g}H^\circ_m$, and $\Delta_{at}H^\circ_m$ denote standard molar energy of combustion, enthalpy of combustion, enthalpy of formation, enthalpy of sublimation, and enthalpy of atomization, respectively.

When comparing the differences between the experimental values for the enthalpy of sublimation at $T = 298.15$ K for the ZnTMPP and the ZnTPP, and for the TMPP and TMPP, a value of 42 kJ·mol^{-1} is obtained in both cases. Furthermore, when comparing the values between ZnTMPP and TMPP as well as the values between ZnTPP and TPP, a difference of 12 kJ·mol^{-1} is observed. Since the trend for the enthalpies of sublimation follows ZnTMPP > TMPP > ZnTPP > TPP, the coordination to Zn(II) ion in both cases increases the intermolecular interactions correspondingly. In addition, the enthalpies of sublimation for free and coordinated TMPP are greater than for free and coordinated TPP. Finally, the experimental Knudsen method at high temperatures appears to be reliable and sensitive for observing molecular structure influences on the values for the enthalpy of sublimation.

When the enthalpies of atomization are compared for the pair TMPP/ZnTMPP, the differences are attributed principally to the contribution of four Zn−N coordination bonds (in ZnTMPP) in relation with two N−H bonds (in TMPP). Using the recommended value of Laidler's parameters[30] for the contribution to the enthalpy of atomization by two N−H bonds, D(N−H) = 377.4 kJ·mol^{-1}, the corresponding value for the Zn−N coordination bond is calculated as D(Zn−N) = (160 ± 9) kJ·mol^{-1} in the ZnTMPP. This value can be compared to that obtained for ZnTPP, D(Zn−N) = (185 ± 6) kJ·mol^{-1}. The differences in these results cannot be attributed to a resonance effect since phenyl substituents are not coplanar to the porphine ring, as observed from the X-ray structures for TPP[31] and ZnTPP.[32] Instead, an inductive effect of the methoxy groups in ZnTMPP could be the reason for the weakness of the Zn−N bond, wholly assessed as (25 ± 11) kJ·mol^{-1} in relation to ZnTPP. The diminishing of Zn−N bond energy in ZnTMPP could favor the axial coordination of water molecules to ZnTMPP at room temperature, as discussed from the observations by DSC.

The large effects that meso substituents have on the π-system of zinc porphyrins have been observed previously by EPR studies.[18] Particularly, differences in half-wave potentials of first oxidation of TPP and ZnTPP are larger than the corresponding to TMPP and ZnTMPP.[19] This has been confirmed when both, ZnTPP and TMPP, are used as catalysts.[33,34] In addition, when they are axially coordinated with 1-methylimidazole, the reaction with ZnTMPP is more exothermic than the reaction with ZnTPP.[35]

The ab initio study of Zwaans et al.[6] suggest that the Zn−N bonds are weaker than the N−H bonds in the porphine ring, as experimentally deduced in the porphyrins studied. The bond energy Zn−N of 55.4 kJ·mol^{-1} obtained in the same study is also consistent with our results because phenyl or methoxyphenyl groups stabilize the porphine ring, leading to stronger Zn−N bonding, when coordinated.

The values for the mean dissociation enthalpies D(N−Zn) of 153, 116, and 116 kJ·mol^{-1}, reported by Chagas and Airoldi[14] and derived from the coordination compounds of $ZnCl_2$ with pyridine, 2,2′-bipyridine, and 1,10-fenantroline, respectively, are weaker than those reported here, because the two coordinated chlorine ions produce a weakness in the Zn−N bonds. In addition a macrocyclic effect in ZnTPP and ZnTMPP is present, increasing the strength of the Zn−N bond in these porphyrins.

Acknowledgment. R. Patiño thanks Conacyt (Mexico) for his scholarship. The authors acknowledge the comments of the reviewers which have improved the original manuscript.

IC0702522

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