Kinetics and Mechanism Study of the Substitution Reactions of the Chloride Ligand in Dichloro(5,10,15,20)-tetraphenyl-21*H*,23*H*-porphinato)tin(IV) by Organic Bases in Dimethylformamide Solvent

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Substitution reactions of a Cl^- ligand in $[SnCl_2(tpp)]$ (tpp = 5,10,15,20-tetraphenyl-21*H*,23*H*-porphinato(2 –)) by five organic bases *i.e.*, butylamine ($BuNH_2$), *sec*-butylamine ($^{s}BuNH_2$), *tert*-butylamine ($^{t}BuNH_2$), dibutylamine (Bu_2NH), and tributylamine (Bu_3N), as entering nucleophile in dimethylformamide at $I = 0.1$M ($NaNO_3$) and 30 – 55° were studied. The second-order rate constants for the substitution of a Cl^- ligand were found to be $(36.86 \pm 1.14) \cdot 10^{-3}$, $(32.91 \pm 0.79) \cdot 10^{-3}$, $(22.21 \pm 0.58) \cdot 10^{-3}$, $(19.09 \pm 0.66) \cdot 10^{-3}$, and $(1.36 \pm 0.08) \cdot 10^{-3}$ $M^{-1}s^{-1}$ at 40° for $BuNH_2$, $^{t}BuNH_2$, $^{s}BuNH_2$, Bu_2NH, and Bu_3N, respectively. In a temperature-dependence study, the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the reaction of $[SnCl_2(tpp)]$ with the organic bases were determined as 38.61 ± 4.79 kJ mol^{-1} and -150.40 ± 15.46 J $K^{-1}mol^{-1}$ for $BuNH_2$, 40.95 ± 4.79 kJ mol^{-1} and -143.75 ± 15.46 J $K^{-1}mol^{-1}$ for $^{t}BuNH_2$, 30.88 ± 2.43 kJ mol^{-1} and -179.00 ± 7.82 J $K^{-1}mol^{-1}$ for $^{s}BuNH_2$, 26.56 ± 2.97 kJ mol^{-1} and -194.05 ± 9.39 J $K^{-1}mol^{-1}$ for Bu_2NH, and 39.37 ± 2.25 kJ mol^{-1} and -174.68 ± 7.07 J K^{-1} mol^{-1} for Bu_3N. From the linear rate dependence on the concentration of the bases, the span of k_2 values, and the large negative values of the activation entropy, an associative (A) mechanism is deduced for the ligand substitution.

Introduction. – Metalloporphyrins are important model compounds that help us understand the biological functions of heme proteins. One of the characteristic features of metalloporphyrins is the acceleration of the axial-ligand-substitution reactions, which is closely related to the biological functions, such as oxygen transport and storage by heme proteins. Such a labilization effect amounts to several orders of magnitude or more in rate, relative to those of cobalt(III) [1 – 14], chromium(III) [14 – 21], rhodium(III) [14][22][23], and ruthenium(III) [24] ions, which are substitution inert. Many studies on the kinetic axial-ligand-substitution reactions of metalloporphyrins have been carried out to elucidate the mechanism of the labilization effect caused by ligation to porphyrins. The general conclusion has been that these reactions are dissociatively activated. This conclusion has been based on the values of the activation parameters: generally, positive or small negative values of $\Delta S^{\ddagger}$ and positive values for $\Delta V^{\ddagger}$ are observed, but for tin(IV) [25] and titanium(IV) [26], the conclusion has been that these reactions are associatively activated.

In this report, the kinetics and mechanism of the substitution of a Cl^- ligand in $[SnCl_2(tpp)]$ (tpp = 5,10,15,20-tetraphenyl-21*H*,23*H*-porphinato(2 –)) by five organic bases, *i.e.*, butylamine ($BuNH_2$), *sec*-butylamine ($^{s}BuNH_2$), *tert*-butylamine ($^{t}BuNH_2$), dibutylamine (Bu_2NH), and tributylamine (Bu_3N) in dimethylformamide (DMF) at $I = 0.1$M ($NaNO_3$) were studied spectrophotometrically and explained by an associative (A) mechanism.

Experimental Part. – *General.* The complex [$SnCl_2$(tpp)] was prepared according to [27]. The VIS absorption spectra were in good agreement with the published ones. All chemicals were used as obtained from *Merck* or *Fluka*, except for the bases from *Merck*, which were distilled before use. Anal. grade solvents from *Merck* were used without further purification.

Kinetic Studies. Substitution rates were determined spectrophotometrically. In all cases (runs from 30–55 ± 0.1°), the procedure involved adding a sample of a given base to a soln. containing the substrate and enough nitrate to maintain ionic strength at 0.1M. Light-absorption measurements in the VIS region were made with a *Jasco-V-530-UV/VIS* spectrophotometer equipped with a *Lauda-ecoline-RE* thermostat. The kinetics was followed at a predetermined wavelength (λ_{kin} 626 nm), where the difference in absorption between the substrate and the product was the largest. The kinetics was followed under pseudo-first-order conditions for base concentrations; the substrate concentration was kept constant at $1 \cdot 10^{-4}$ M, and the excess concentration of each base was varied in the range 0.0025–0.0700 M (*Tables 1–4*). The temp. was controlled in a thermostated cell compartment at 30–55 ± 0.1°, and 10-mm quartz cells were used. The pseudo-first-order constants were calculated by fitting the data to $\ln[(A - A_0)/(A - A_t)] = k_{obs}t$ by means of a linear least-squares computer program. The second-order rate constants were obtained from the slope of the linear plots of k_{obs} *vs.* [B] (base conc.). $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained from *Eyring* plots of $\ln(k_2/T)$ *vs.* $1/T$ at four different temp. in the range 30–55°.

Table 1. *Pseudo-First-Order Rate Constants* $k_{obs} \cdot 10^{4}$[a]) *for the Reaction of [*$SnCl_2$*(tpp)] with* $BuNH_2$ *at* I = *0.1*M *in DMF at Different Temperatures.* [Complex] = 0.0001M.

T/°	$BuNH_2$/M									$k_2 \cdot 10^3$/M^{-1} s^{-1}
	0.0025	0.0050	0.0075	0.0100	0.0125	0.0150	0.0200	0.0250	0.0300	
30.0	0.56(0.00)	0.98(0.01)	1.57(0.01)	2.13(0.00)	2.63(0.01)	3.08(0.01)	4.00(0.01)	5.20(0.00)	5.88(0.00)	19.81(0.38)
35.0	0.77(0.01)	1.65(0.00)	2.55(0.01)	3.22(0.01)	3.90(0.00)	4.59(0.00)	5.53(0.00)	6.80(0.01)	8.43(0.02)	26.50(0.80)
40.0	1.01(0.01)	2.00(0.01)	2.76(0.01)	3.38(0.01)	4.37(0.01)	5.55(0.01)	7.84(0.01)	9.54(0.00)	10.71(0.01)	36.86(1.14)
45.0	1.33(0.01)	2.46(0.00)	3.63(0.01)	4.85(0.00)	5.41(0.00)	6.71(0.01)	8.86(0.02)	10.51(0.03)	13.07(0.14)	41.74(0.70)

[a]) The numbers in parentheses are the standard deviations of k_{obs}.

Table 2. *Pseudo-First-Order Rate Constants* $k_{obs} \cdot 10^{4}$[a]) *for the Reaction of [*$SnCl_2$*(tpp)] with* $^tBuNH_2$ *at* I = *0.1*M *in DMF at Different Temperatures.* [Complex] = 0.0001M.

T/°	$^tBuNH_2$/M									$k_2 \cdot 10^3$/M^{-1} s^{-1}
	0.0025	0.0050	0.0075	0.0100	0.0125	0.0150	0.0200	0.0250	0.0300	
30.0		0.89(0.00)	1.39(0.01)	1.77(0.00)	2.38(0.00)		3.62(0.00)	4.42(0.00)	5.14(0.01)	17.11(0.39)
35.0		1.58(0.00)	2.41(0.00)	3.14(0.00)	3.81(0.00)	4.50(0.01)	5.34(0.00)	6.61(0.02)	7.71(0.03)	23.84(0.79)
40.0	0.59(0.00)	1.64(0.00)	2.55(0.01)	3.35(0.00)	4.09(0.00)	4.67(0.00)	6.69(0.01)	8.09(0.00)		32.91(0.76)
45.0	1.14(0.01)	2.24(0.00)	3.20(0.01)	4.71(0.00)	5.75(0.01)	6.76(0.00)	8.34(0.03)	9.79(0.03)	11.68(0.08)	37.95(1.43)

[a]) The numbers in parentheses are the standard deviations of k_{obs}.

Table 3. *Pseudo-First-Order Rate Constants* $k_{obs} \cdot 10^{4}$[a]) *for the Reaction of [*$SnCl_2$*(tpp)] with* Bu_2NH *at* I = *0.1*M *in DMF at Different Temperatures.* [Complex] = 0.0001M.

T/°	Bu_2NH/M										$k_2 \cdot 10^3$/M^{-1} s^{-1}
	0.0010	0.0025	0.0050	0.0075	0.0100	0.0150	0.0200	0.0250	0.0300	0.0350	
30.0	0.17(0.00)	0.47(0.00)	1.06(0.00)	1.48(0.00)	1.70(0.00)	2.17(0.00)	2.37(0.01)				19.81(0.38)
35.0		0.53(0.00)	1.16(0.01)	1.65(0.01)	2.00(0.00)	2.70(0.02)	3.50(0.00)	4.90(0.01)	5.70(0.02)	7.00(0.00)	19.09(0.66)
40.0		0.61(0.00)	1.31(0.00)	1.69(0.00)	2.11(0.00)	3.20(0.00)	4.21(0.01)	5.56(0.02)	6.67(0.01)	7.93(0.03)	22.20(0.46)
45.0		0.63(0.00)	1.51(0.01)	2.18(0.00)	2.80(0.00)	3.72(0.01)	4.90(0.00)	6.84(0.00)	7.75(0.00)	9.00(0.01)	25.37(0.69)

[a]) The numbers in parentheses are the standard deviations of k_{obs}.

Table 4. *Pseudo-First-Order Rate Constants* $k_{obs} \cdot 10^5$[a]) *for the Reaction of* $[SnCl_2(tpp)]$ *with* Bu_3N *at* I = 0.1M *in DMF at Different Temperatures.* [Complex] = 0.0001M.

T/°	Bu_3N/M									$k_2 \cdot 10^3$/M^{-1} s^{-1}
	0.0300	0.0350	0.0400	0.0450	0.0500	0.0550	0.0600	0.0650	0.0700	
40.0	1.71(0.01)[a]	2.10(0.01)	2.46(0.00)	3.33(0.02)	3.83(0.05)	4.29(0.02)	5.74(0.06)	6.30(0.04)	6.89(0.02)	1.36(0.08)
45.0	2.40(0.02)	2.84(0.02)	3.55(0.02)	5.36(0.06)	6.32(0.02)	6.65(0.04)	7.68(0.03)	8.48(0.03)	9.34(0.04)	1.81(0.09)
50.0	2.70(0.01)	4.17(0.01)	5.81(0.01)	6.83(0.01)	7.87(0.01)	8.48(0.03)	9.38(0.04)			2.19(0.15)
55.0	3.06(0.01)	5.01(0.02)	6.68(0.01)	7.79(0.01)	9.62(0.01)	10.75(0.01)				2.90(0.12)

[a]) The numbers in parentheses are the standard deviations of k_{obs}.

Results and Discussion. – *Table 5* shows the rate constants and the activation parameters for the entry of organic bases into the $[SnCl_2(tpp)]$ in DMF as solvent at constant ionic strength (0.1M $NaNO_3$) and at a number of temperatures. The k_2 values are obtained from the linear plots of k_{obs} *vs.* the base concentration [B] (see *Fig. 1*). The rate law of *Eqn. 1* is compatible with the transformations according to *Eqns. 2* and *3*.

$$k_{obs} = k_2[B] \tag{1}$$

$$[SnCl_2(tpp) + B \xrightarrow{k_2} [SnCl_2(tpp)(B)] \text{ slow} \tag{2}$$

$$[SnCl_2(tpp)(B) \longrightarrow [SnCl(tpp)(B)]^+ + Cl^- \text{ fast} \tag{3}$$

Table 5. *Second-Order Rate Constants* k_2 *and Activation Parameters* $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, *and* $\Delta G^{\ddagger}$ *of Reactions of* $[SnCl_2(tpp)]$ *with Organic Bases* (B) *in DMF at* I = *0.1*M. Standard deviations in parentheses.

	T/°	$k_2 \cdot 10^2$/M^{-1} s^{-1}[a])	$\Delta H^{\ddagger}$/kJ/mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1}mol^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}[b])
$BuNH_2$	30	19.81(0.38)			
	35	26.50(0.80)			
	40	36.85(1.14)			
	45	41.74(0.70)	38.61(4.79)	– 150.40(15.46)	85.69(6.81)
$^tBuNH_2$	30	17.11(0.39)			
	35	23.84(0.79)			
	40	32.91(0.76)			
	45	37.95(1.43)	40.95(4.79)	– 143.75(15.46)	85.94(6.81)
$^sBuNH_2$	30	13.84(0.40)			
	35	17.34(0.38)			
	40	22.21(0.58)			
	45	25.54(0.73)	30.88(2.43)	– 179.00(7.82)	86.91(3.45)
Bu_2NH	35	14.84(0.71)			
	40	19.09(0.66)			
	45	22.20(0.46)			
	50	25.38(0.69)	26.56(2.97)	– 194.05(9.39)	87.30(4.18)
Bu_3N	40	1.36(0.08)			
	45	1.81(0.09)			
	50	2.19(0.15)			
	55	2.90(0.12)	39.37(2.25)	– 174.68(7.07)	94.09(3.16)

[a]) k_2 is the slope of linear plots of k_{obs} *vs.* [B]. [b]) At 40°.

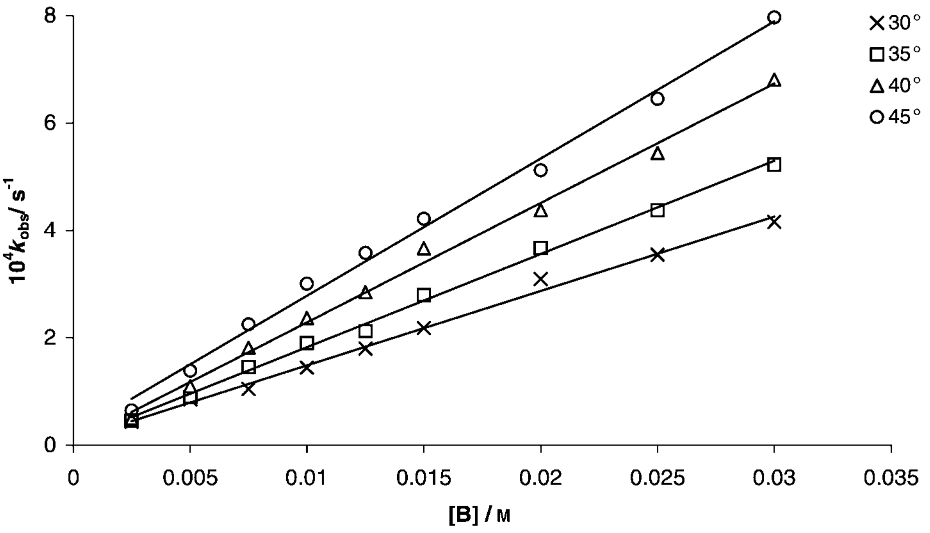

Fig. 1. *Plots of* k_{obs} vs. *^{s}BuNH$_2$ molar concentrations [B] at different temperatures.* $I = 0.1$M in DMF.

The reaction involves nucleophilic attack by a base to produce a seven-coordinated intermediate (*Eqn. 2*). Numerous complexes of tin(IV) with coordination number seven have been characterized [28–32], establishing that the Sn-atom can – by expanding its coordination sphere – form complexes with coordination number greater than six under certain conditions. Thus, a seven-coordinated intermediate formed in an associative mechanism on substitution of a Cl^- ligand by an organic base can reasonably be suggested. Also, there are some reports indicating an associative mechanism for tin(IV) [25] and titanium [26] complexes. Presumably, this mechanism is due to the presence of empty 5d orbitals in the Sn-atom and to the bulkiness of the Sn-atom.

The isosbestic points observed at 40° for the reaction with $BuNH_2$ were at 375, 401, 518, 546, 573, and 641 nm (*Fig. 2*), with ^{t}BuNH$_2$ at 352, 521, 543, 572, and 646 nm, with ^{s}BuNH$_2$ at 364, 520, 545, 571, and 643 nm, with Bu_2NH at 360, 448, 528, 544, 574, and 652 nm, and with Bu_3N at 358, 440, 576, and 650 nm. These data show that the organic bases have substituted only one Cl^- ligand in the substrate. The second Cl^- substitution is possibly so slow that it does not interfere with the first substitution.

Also the stability of the substrate [$SnCl_2$(tpp)] in DMF was tested, and it was shown that the substitution of Cl^- by DMF was so slow that it did not interfere with the reaction of organic bases. Therefore, the latter was not preceded by solvent intervention.

The activation parameters $\Delta S^{\neq}$ and $\Delta H^{\neq}$ (*Table 5*) were obtained from the standard linear *Eyring* plots of $\ln(k_2/T)$ *vs.* $1/T$ with a good correlation of 0.97–0.99 (*Fig. 3*). The reaction steps of *Eqns. 2* and *3* are $\Delta H^{\neq}$- and $\Delta S^{\neq}$-dependent.

The isokinetic plot (*Fig. 4*) has a slope corresponding to the isokinetic temperature −17.3° which suggests that all the systems studied in this work follow the same mechanism. The results shown in *Tables 1–5* for the five bases establish that there is a

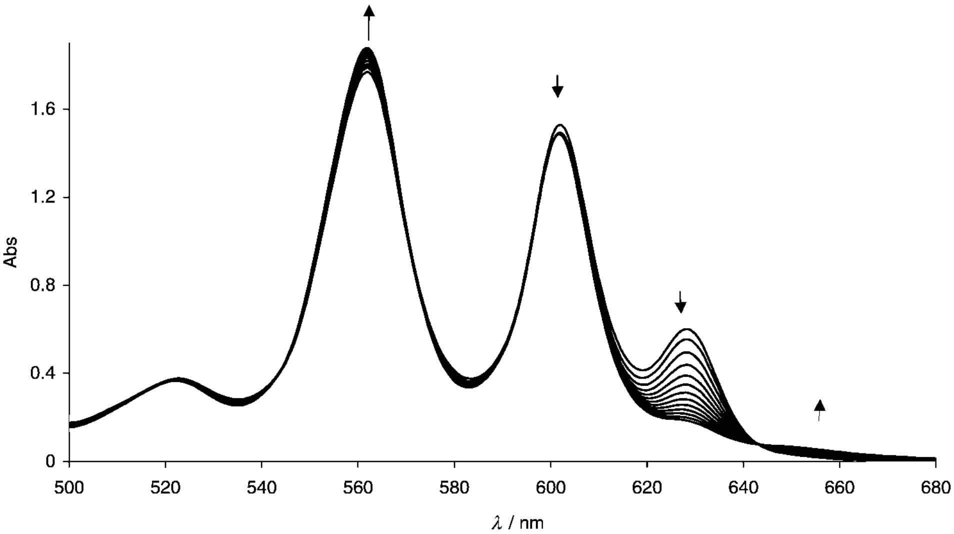

Fig. 2. *Absorption spectra of [$SnCl_2$(tpp)] in the presence of $BuNH_2$ at 40° in DMF with the isosbestic points*

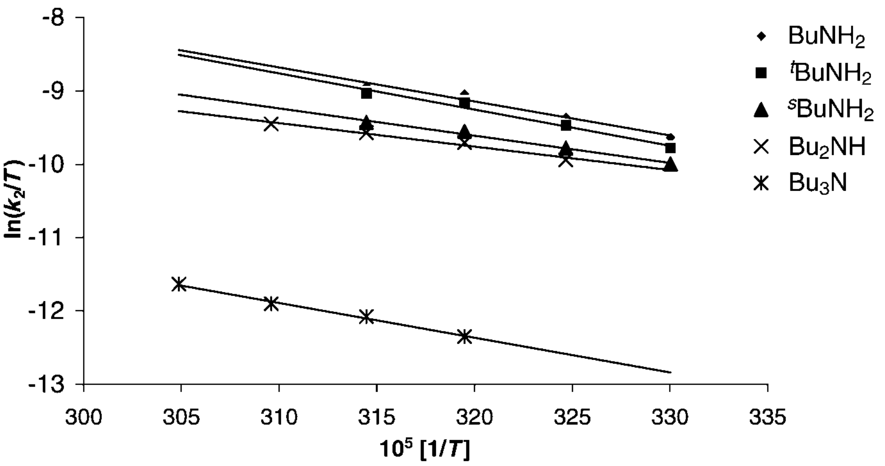

Fig. 3. Eyring *plots for reactions of different bases with [$SnCl_2$(tpp)] in DMF*

linear rate dependence on the concentration [B] of the bases. The linear plots of k_{obs} *vs.* [B], the span of k_2 values, and the large negative values of $\Delta S^{\neq}$ possibly suggest an associative (A) mechanism.

The nucleophilicity trend of the organic bases toward the substrate is as follows: $BuNH_2 > {}^tBuNH_2 > {}^sBuNH_2 > Bu_2NH > Bu_3N$ ($k_2 \cdot 10^3$ M^{-1} s^{-1}: 36.86 > 32.91 > 22.21 > 19.09 > 1.36). The reactivity order of the organic bases toward the substrate is roughly determined by their steric rather than by their basic characters. When the steric hindrance increases (primary < secondary < tertiary amines), the tendency to react with the substrate decreases. The steric hindrance being similar in the case of primary

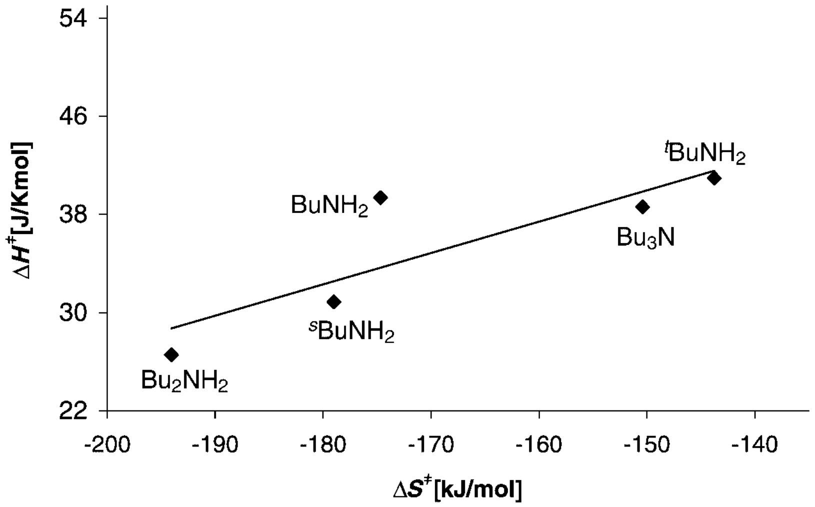

Fig. 4. *Isokinetic plot for bimolecular reactions of [$SnCl_2$(tpp)] with different organic bases in DMF*

amines, the basicity determines which amine is more reactive, in accordance with $K_b = 4.8 \cdot 10^{-4}$ for $BuNH_2$, $5.0 \cdot 10^{-4}$ for $^{t}BuNH_2$, and $4.0 \cdot 10^{-4}$ for $^{s}BuNH_2$ in H_2O [33][34]. The basicities of $BuNH_2$ and $^{t}BuNH_2$ are similar ($K_b = 4.8 \cdot 10^{-4}$ and $5.0 \cdot 10^{-4}$, resp.), and the sterically less-hindered $BuNH_2$ has a greater tendency to associate with the substrate [34]. However, the basicity of organic bases is determined by steric, induction, and solvation factors [35].

We are grateful to Shiraz University Research Council for its financial support. Thanks are also due to *B. Hemattinejhad* for writing the modified computer program.

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Received February 25, 2002