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Effect of Steric Strains in the Macroring on the Structure and Properties of Molecular Complexes of (Chloro)[5,15-(*p*-butoxyphenyl)-2,8,12,17-tetramethyl-3,7,13,17-tetrabutylporphinato]aluminum

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Abstract—The chelate (Cl)AlP was prepared by complexation of porphine (*P*) with aluminum(III) chloride in refluxing pyridine. Equilibrium coordination of nitrogen-containing ligands (L = 2-methylimidazole, imidazole, pyridine, 3,5-dimethylpyrazole, dimethylformamide) with (Cl)AlP in benzene was studied by spectrophotometric titration and computer simulation. Quantitative and qualitative characteristics of the reaction were obtained. The structure of the mixed-ligand complex formed by intermolecular interaction of the metal porphyrin with a base was determined spectrophotometrically and by quantum-chemical calculations. An effect of additional molecular ligand and of steric strain in the macroring on the stability of the complex was noted. The stability constant (K_s) increases with an increase in the basicity (K_{BH^+}) of the extra ligand and is proportional to the shift of the main bands ($\Delta\lambda$) in the electronic absorption spectra. The geometric and energy characteristics of hexacoordinated aluminum porphyrin were calculated by the PM3 method. Correlations were found between the calculated energy of the interaction of the aluminum atom with the base molecule (E_b) and stability of the mixed-ligand complexes (Cl)Al(L)P. The *cis* and *trans* effects in the complexes (Cl)Al(L)P were analyzed. The dependence of the strength of the Al–L bond on the nature of the porphyrin and the basicity of the additional molecular ligand was determined from the experimental data and calculation results.

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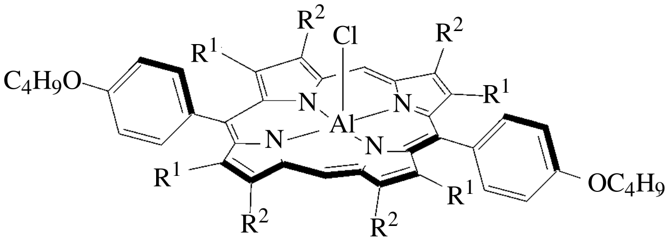
Growing interest in macrocyclic complexes with highly charged metal cations is primarily due to the possibility of their use as redox catalysts [1–4].

One of elementary reactions in catalysis is extra coordination [3, 4]. To develop effective catalysts, it is necessary to study this reaction in detail with simple model systems metal porphyrin–base. However, such reactions have not been comprehensively studied up to now.

To study systematically the influence of the structure of porphyrin and nature of the central metal atom on the coordination properties of macrocyclic compounds, we examined in this study the interaction of (chloro)[5,15-(*p*-butoxyphenyl)-2,8,12,17-tetramethyl-3,7,13,17-tetrabutylporphinato]aluminum (Cl)AlP with nitrogen-containing bases (2-methylimidazole, 2-MeIm; imidazole, Im; pyridine, Py; 3,5-dimethylpyrazole, DMP; dimethylformamide, DMF) in benzene.

The interactions were studied by spectrophotometric titration [5] and computer simulation [6–8].



(Cl)AlP, R^1 = C$_4$H$_9$; R^2 = CH$_3$.

Spectrophotometric titration data show that the coordination of nitrogen-containing bases L with aluminum porphyrin occurs in one step and virtually instantaneously. Formation of the Al–L bond in the macroring, as in the complex of zinc with a similar porphyrin [9], is accompanied by a bathochromic shift and a change in the intensity of the main absorption bands of the chromophore (Fig. 1) [10]. Such changes in the electronic spectrum of the metal porphyrin are associated, as a rule, with an increase in the electron density on the central metal atom and, correspondingly, on the nitrogen atoms of the porphyrin, with the destabilization of the molecular orbital a_{2u}, no change

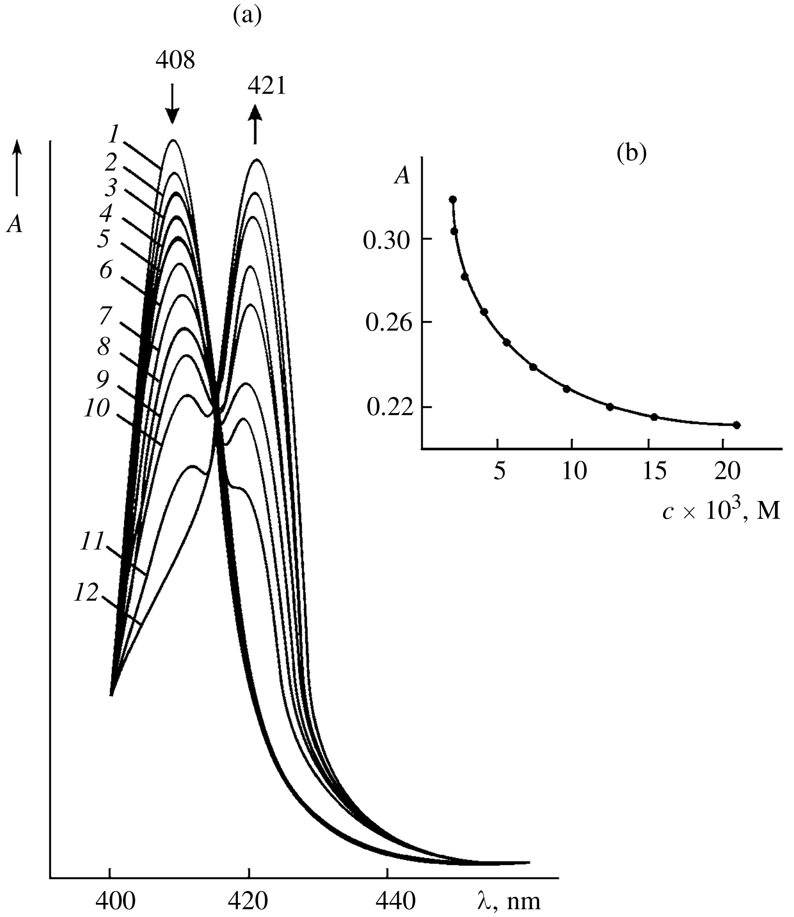


Fig. 1. (a) Variation of the electronic absorption spectrum of (Cl)AlP in benzene with addition of imidazole. Imidazole concentration, M: (*1*) 0 and (*12*) 6.3×10^{-2}; (*2–11*) intermediate concentrations. (b) Curve of spectrophotometric titration of (Cl)AlP with imidiazole (λ = 407 nm).

in the level of a_{1u}, and decrease in the configuration interaction of the excited state of the E_u type [10].

The intermolecular interaction of the macrocyclic compound with the nitrogen-containing base yields a complex (Cl)Al(L)P [metal porphyrin coordinates one base molecule (Fig. 2)].

From data in Table 1, we estimated the stability of the molecular complexes, which increases in the order (Cl)Al(DMF)P < (Cl)Al(DMP)P < (Cl)Al(Py)P < (Cl)Al(2-MeIm)P < (Cl)Al(Im)P. With an increase in temperature by 20 K, this order is not altered, but the stability constants decrease by a factor of 1.6–2. We found correlations between K_s, basicity of the extra ligand (characterized by pK_{BH^+} and determined potentiometrically in water at 298 K [11]), and shift ($\Delta\lambda$) of the main absorption bands in the electronic absorption spectra of the complexes (Table 1). The correlations obtained, in contrast to the similar dependences for the complexes (Cl)AlTPP (TPP is *meso*-tetraphenylporphine), are ascending and are described by the equations $\log K_s = 1.2583 + 0.0002pK_{BH^+}$ ($r = 0.971$) and $\log K_s = 0.0189\Delta\lambda^2 - 0.098\Delta\lambda + 1.2428$ ($r = 0.997$), respectively. It should be noted that the linearity of the dependences is disturbed owing to an in-

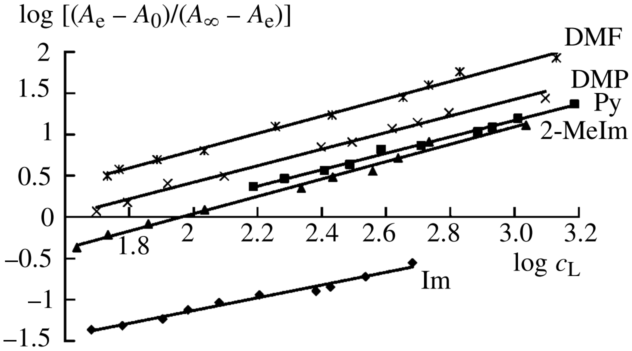


Fig. 2. Plots of $\log[(A_e - A_0)/(A\infty - A_e)]$ vs. $\log c_L$ for the intermolecular interaction of (Cl)AlP with nitrogen-containing bases in benzene.

Table 1. Thermodynamic parameters of the intermolecular interaction of (chloro)[5,15-(*p*-butoxyphenyl)-2,8,12,17-tetramethyl-3,7,13,17-tetrabutylporphinato]aluminum with nitrogen-containing bases in benzene

Extra ligand	K_s, l mol^{-1}			log K_s (298 K)	pK_{BH^+}	Δλ, nm	–Δ*H*, kcal	–Δ*S*, kcal
	298 K	308 K	318 K					
Im	1510.0±295.0	904.0±90.40	609.0±60.90	3.1789	6.65	13	8.557	14.17
2-MeIm	124.0±11.40	90.3±10.60	66.9±3.23	2.0934	5.89	10	5.809	9.92
Py	88.3±10.30	62.2±6.49	39.8±2.94	1.9459	5.29	9	7.489	16.23
DMP	37.9±4.15	26.9±5.66	19.5±3.96	1.5786	4.27	7.5	6.256	13.77
DMF	15.1±1.63	10.2±0.85	7.7±1.24	1.1789	0.92	4.5	6.361	15.95

crease in the steric strain of the macroring in the metal porphyrin [12].

With an increase in the deformation of the porphyrin in going from (Cl)AlTPP to (Cl)AlP, the aromaticity of the macroring decreases and, as a result, its basicity increases. A decrease in the number of phenyl substituents and introduction of alkyl groups into β positions of the macroring also lead to an increase in the basicity. As a result, the stability of molecular complexes of (Cl)Al(L)P becomes 2–3 times lower than the stability of (Cl)Al(L)TPP (Table 1, [12]).

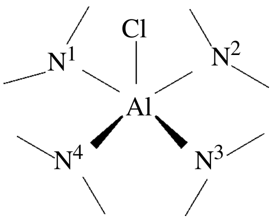
It is interesting that, despite higher formal charge and small ionic radius, aluminum porphyrin (Cl)AlP forms less stable complexes than its zinc analog [9]. In this case, the stability is influenced not only by the macroring strain but also by the presence of the acido ligand in the mixed-ligand complx (Cl)Al(L)P. It should be noted that the Al–Cl bond, which is largely covalent, decreases the effective positive charge on the Al atom, which also results in destabilization of the molecular complexes of the aluminum porphyrin.

From the experimental data, we determined the thermodynamic characteristics of the intermolecular interaction (Δ*H*, Δ*S*). The complexation of (Cl)AlP with L is an exothermic reaction with low negative values of Δ*S* (Table 1). The negative entropy characterizes a decrease in the number of the reacting species and an increase in the ordering in the system.

By the PM3 quantum-chemical method, we optimized the structures of (Cl)AlP and its molecular complexes and determined the geometric and energy characteristics of the complexes.

The compound (Cl)AlP has a pyramidal structure of the coordination core with a rhombic base, with approximate symmetry C_{4v} (Scheme 1). This conclusion is well consistent with X-ray structural data [10].

Scheme 1.



Comparison of the optimized structure of (Cl)AlP with the averaged structure of metal porphyrins with the lowest internal stresses of the macroring [10, 13] shows that the molecule of (Cl)AlP has a nonplanar distorted structure. The Al atom is shifted to one of the *meso*-C atoms and deviates from the mean N_4 plane by 0.4985 Å toward the acido ligand. The pyrrole fragments are inclined alternately up and down (Fig. 3). The macroring is unsymmetrical: The distances between the opposite internal N atoms (N^1–N^3, N^2–N^4) and between the opposite external carbon atoms (C^{m1}–C^{m3}, C^{m2}–C^{m4}) are not equal (Table 2). The geometries of the pyrrole rings are also different: Four CNC bond angles are 107.25°, 107.09°, 108.73°, and 108.52°. The skeleton atoms of the porphyrin macroring deviate from the mean molecular plane (Fig. 4).

The total effective charge (q_{eff}) on the coordinated N atoms is –0.172 e, and the charge on the metal atom is +0.621 e.

In molecular complexes of (Cl)AlP with nitrogen bases, the coordination core becomes bipyramidal (Scheme 2). Such changes are accompanied by an

Scheme 2.

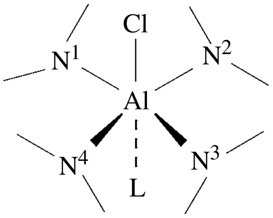
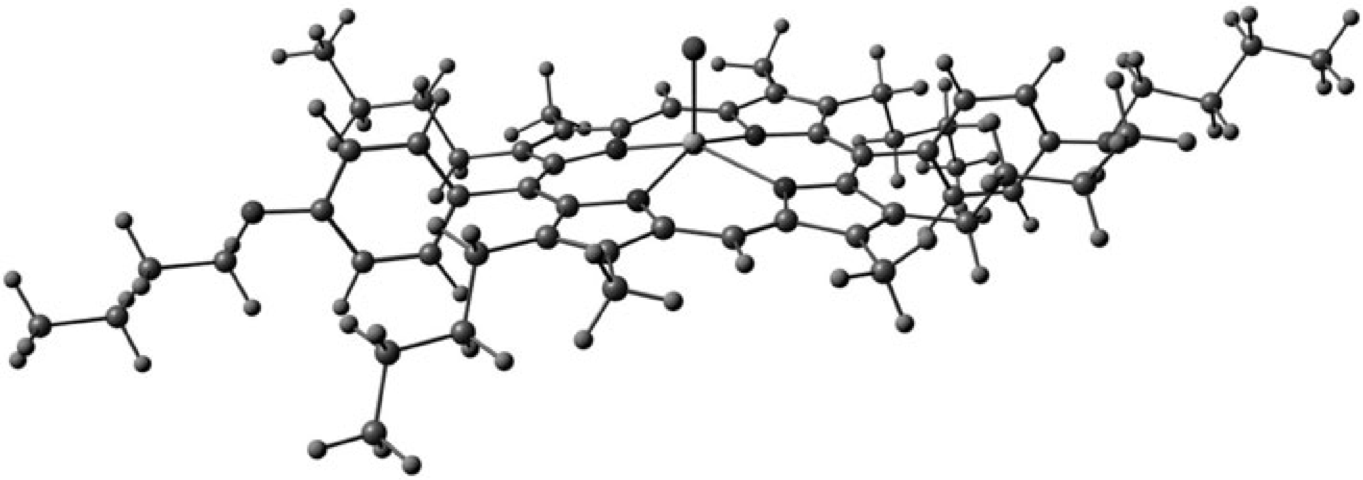


Table 2. Some geometric and energy characteristics of molecular complexes of (chloro)[5,15-(*p*-butoxyphenyl)-2,8,12,17-tetramethyl-3,7,13,17-tetrabutylporphinato]aluminum

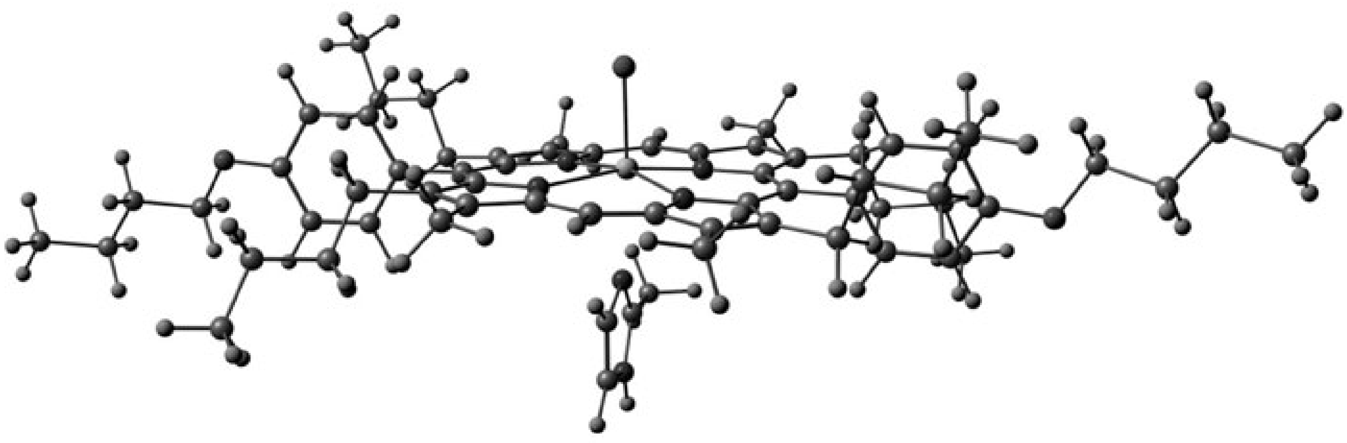
Extra ligand	E_b, kcal mol^{-1}	Interatomic distances, Å							
		N^1–N^3	N^2–N^4	$l_{\text{av. Al–Np}}$	Al–L	Al–Cl	Al–Ct	C^{m1}–C^{m3}	C^{m2}–C^{m4}
–	–	4.1300	4.1407	2.1299	–	2.3047	0.4685	7.2185	6.6757
Im	–9.13	4.1689	4.1902	2.1242	2.4984	2.3439	0.3847	7.2381	6.6745
2-MeIm	–7.03	4.1701	4.1888	2.1218	2.5212	2.3489	0.3685	7.2389	6.6707
Py	–4.99	4.1671	4.1909	2.1235	2.5217	2.3431	0.3672	7.2423	6.6708
DMP	–2.45	4.1653	4.1856	2.1214	2.5476	2.3461	0.3637	7.2402	6.6725
DMF	9.59	4.1581	4.1945	2.1188	2.6498	2.3513	0.3402	7.2383	6.6769

increase in the in-plane and torsion strains in the metal porphyrin (Table 2; Figs. 3, 4).

According to the calculations, the molecular complexes of the sterically strained aluminum porphyrin have structures of the type (Cl)Al(L)P. This result is well consistent with the experimental data. The base molecule is coordinated from the side opposite to the acido ligand (Fig. 3).



(Cl)AlP



(Cl)Al(2-MeIm)P

Fig. 3. Structure of (chloro)[5,15-(*p*-butoxyphenyl)-2,8,12,17-tetramethyl-3,7,13,17-tetrabutylporphinato]aluminum and its molecular complex with 2-methylimidazole, calculated by the PM3 method.

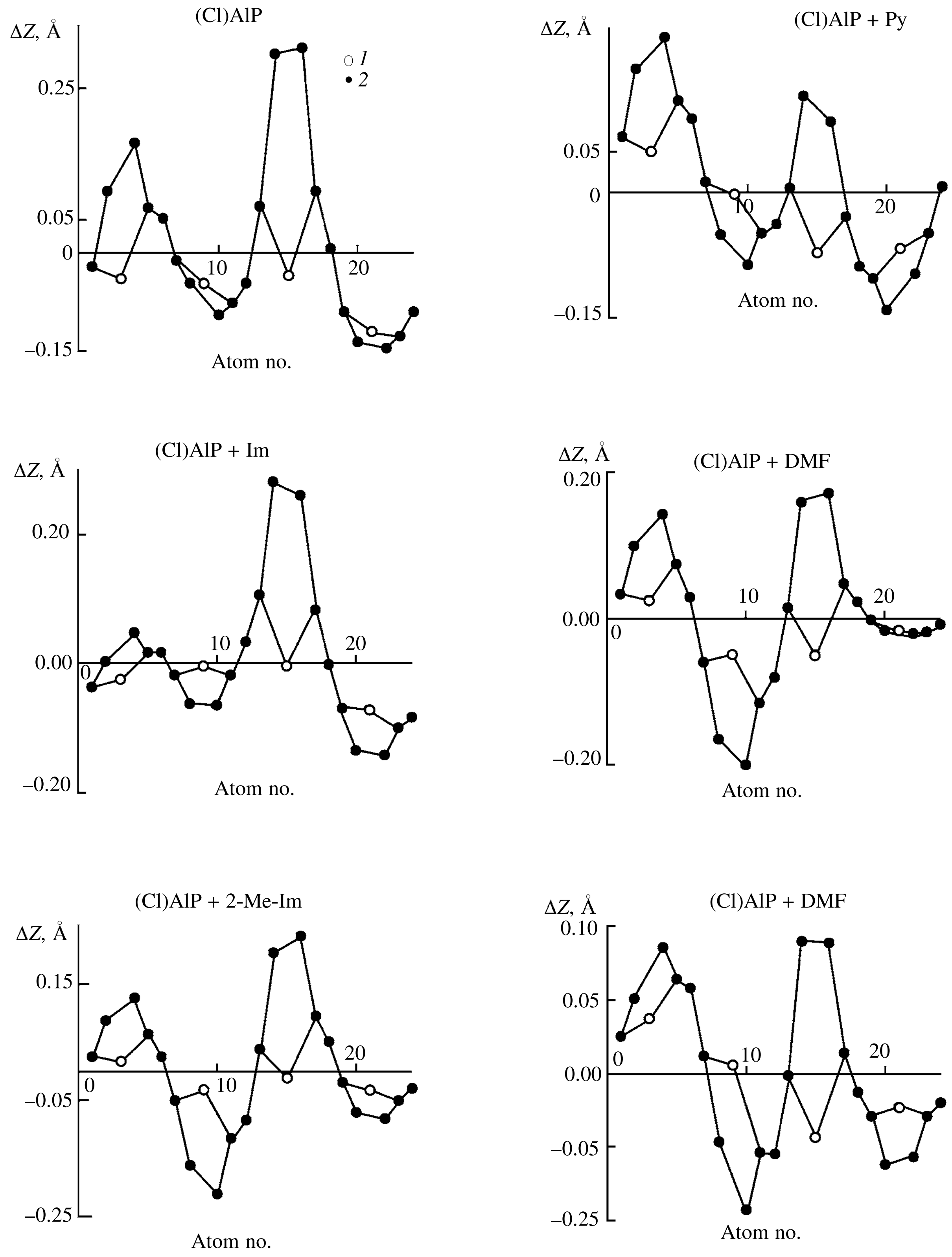


Fig. 4. Deviation ΔZ from the mean molecular plane of the skeleton atoms of the porphyrin macroring in (chloro)[5,15-(*p*-butoxyphenyl)-2,8,12,17-tetramethyl-3,7,13,17-tetrabutylporphinato]aluminum and its molecular complexes with nitrogen-containing bases, according to PM3 calculations. (*1*) N and (*2*) C atoms.

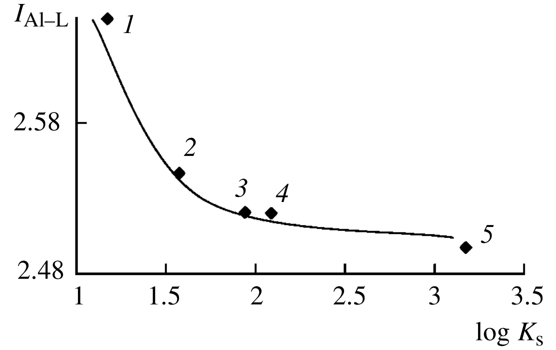


Fig. 5. Correlation between the Al–L bond length and stability of the molecular complex: (*1*) (Cl)Al(DMF)P, (*2*) (Cl)Al(DMP)P, (*3*) (Cl)Al(Py)P, (*4*) (Cl)Al(2-MeIm)P, and (*5*) (Cl)Al(Im)P.

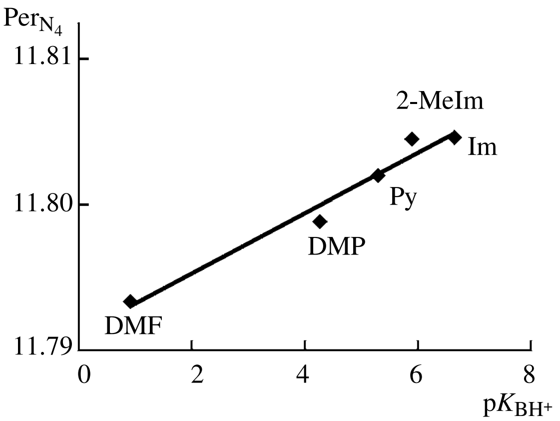


Fig. 6. Correlation between the perimeter of the N_4 coordination plane of the macroring and pK_{BH^+} of the nitrogen-containing base.

Formation of the molecular complexes is accompanied by an increase in the size of the coordination cavity N_4 (Table 2) and in the effective charge on N atoms by 0.055–0.113 e. The charge of the metal atom decreases by 0.019–0.034 e. The deviation of the Al atom from the N_4 plane (Al–Ct) decreases in the order Im > 2-MeIm ≥ Py > DMP > DMF. In the case of sterically strained (Cl)AlTPP, the trend is opposite [12]. For (Cl)Al(L)TPP and (Cl)Al(L)P, the correlations between the length of the Al–L bond in the complex and its stability are largely similar. The stronger the Al–L bond, the higher K_s (Tables 1, 2). However, as in the above-described cases, for (Cl)Al·(L)P, in contrast to (Cl)Al(L)TPP, the correlation is nonlinear: $l_{Al–L} = 2.502(1 - e^{-2.607 \log K_s}) - 1.208$, $r = 0.994$ (Fig. 5).

We found that the Al–L bond length correlates with the Al–Ct distance (Table 2). The correlation is ascending and is described by the equation $l_{Al–L} = 62.563(l_{Al–Ct})^2 - 48.792 l_{Al–Ct} + 12.009$, with the correlation coefficient $r = 0.9909$. The perimeter of the N_4 coordination plane of the macroring (Per_{N_4}) of molecular complexes linearly correlates with the basicity of the extra ligand: $Per_{N_4} = 0.0017 pK_{BH^+} + 11.791$, $r = 0.9686$ (Fig. 6). The size of the N_4 plane in the molecular complex increases with an increase in pK_{BH^+} of the extra ligand.

We found that the strength of the Al–N_P σ bond in aluminum porphyrins decreases in the series of bases DMF > DMP > 2-MeIm > Py > Im (Table 2). In this case, the interaction of the aluminum atom with the nitrogen atom of the extra ligand becomes weaker; as a result, the stability of the metal porphyrin decreases (Tables 1, 2). Thus, the *cis* effect of ligands in the extra complexes is fairly strong. The occurrence of the *trans* effect in the molecular complexes is confirmed by variation of the Al–Cl and Al–Ct distances and by an increase in the negative charge on Cl (by 0.047–0.065 e), observed with formation of the Al–L bond (Table 2).

The calculation results obtained show that the energy consumption (E_b) for formation of a bond between the Al atom and the N atom of the base increases in the order (Table 2) (Cl)Al(Im)P < (Cl)Al(2-MeIm)P < (Cl)Al(Py)P < (Cl)Al(DMP)P < (Cl)Al(DMF)P. The stability of the molecular complex correlates with E_b (FIg. 7): $\log K_s = -0.0014(E_b)^2 + 0.022E_b + 0.4107$, with the correlation coefficient $r = 0.982$. An increase in E_b corresponds to a decrease in the Al–L bond strength.

The good agreement between the experimental and calculated data (Tables 1, 2) allows the use of computer simulation for predicting characteristics of the extra coordination reaction and the structures of the molecular complexes.

Our results show that the stability of metal porphyrin extra complexes depends on the nature of the extra ligand and central metal atom and on the structure and extent of steric strain of the macroring. Formation of molecular complexes is accompanied by changes in the electronic and geometric structure and, as a consequence, by an increase in the steric strain of aluminum porphyrin.

EXPERIMENTAL

The complexation equilibrium, (Cl)AlP + nL = (Cl)Al(L)$_n$P, was studied in benzene at 298, 308, and 318 K.

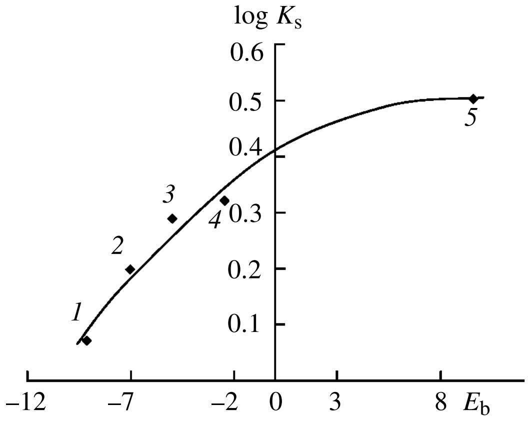


Fig. 7. Correlation of the stability of molecular complexes (Cl)Al(L)P with E_b: (*1*) (Cl)Al(Im)P, (*2*) (Cl)Al · (2-MeIm)P, (*3*) (Cl)Al(Py)P, (*4*) (Cl)Al(DMP)P, and (*5*) (Cl)Al(DMF)P.

Variation of the electronic absorption spectrum of the metal porphyrin with varying the extra ligand concentration allows spectroscopic monitoring of the extra coordination. Measurements were performed at λ = 407 nm. The electronic absorption spectra were recorded on SF-26 and Specord M-400 spectrometers, and the ^{1}H NMR spectra, on a Bruker AC-200 spectrometer (200 MHz, external reference HMDS) in $CDCl_3$. The experimental procedure and the procedure for calculating the stability constants of the extra complexes (K_s) are described in detail in [5, 14–17]. The number of the added ligands was determined by the Bent–French method [5].

The quantities ΔH and ΔS for the extra complexation were determined by least-squares treatment of the dependences of $-\ln K_s$ on $1/T$.

Quantum-chemical calculations were performed by the PM3 method [6–8] with full geometry optimization. The calculations were performed until a preset gradient, 0.06 kJ mol^{-1} Å^{-1}, was attained. The PC version [18] of the Gamess program package [19] was used. Preparation of the initial data and processing of the results of geometry calculation were performed using ChemCraft program (author A.A. Zhurko). In the starting approximation, we used for the porphyrin macroring the bond angles and lengths in the averaged structure of metal porphyrins [10]; the bond lengths and angles in phenyl and alkyl substituents of the porphyrin and in nitrogen bases were taken from [20]. The butyl substituents in the starting approximation were set in the form of *trans* isomers in the staggered conformation. The mean plane of the phenyl fragments was oriented at a right angle relative to the mean plane of the macroring. The orientation of aromatic bases was set so that the mean plane of the extra ligand was perpendicular (for dimethylformamide, parallel) to the mean plane of the porphyrin macroring, and the nitrogen atom with the lone electron pair was directed toward the coordination center. The orientation of the mean plane of the extra ligand relative to phenyl substituents was varied with a step of 30°; in the course of calculations, the mean planes of the base (except dimethylformamide) and phenyl fragments became virtually parallel in all the cases.

5,15-(*p*-Butoxyphenyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin was prepared by condensation of the corresponding dipyrrolylmethane with *p*-butoxybenzaldehyde, following published protocols [21–23]. Electronic absorption spectrum (chloroform), λ_{max}, nm (log ε): 632.0 (3.72), 549.0 (3.80), 517.0 (4.12), 413.0 (5.10). ^{1}H NMR spectrum, δ, ppm: 10.07 (m”s°-H), 2.79 m (Bu–H), 3.39 s (Me–H),4.00 m (OCH_2), –2.27 s (NH).

(Chloro)[5,15-(*p*-butoxyphenyl)-2,8,12,17-tetramethyl-3,7,13,17-tetrabutylporphinato]aluminum. A 10-mg portion of 5,15-(*p*-butoxyphenyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin was dissolved in 30 ml of anhydrous porphyrin, and a 50-fold excess of $AlCl_3$ was added. The mixture was refluxed for 6 h. After cooling, the complex was precipitated by adding 100 ml of water and 30 ml of acetic acid, filtered off, washed with warm water, dissolved in a minimal amount of $CHCl_3$, and chromatographed on alumina (Brockmann grade II, eluent $CHCl_3$). After repeated chromatographic purification, the dry complex was isolated by removing $CHCl_3$ in a vacuum; yield 61%. Electronic absorption spectrum (benzene), λ_{max}, nm (log ε): 578.0 (4.48), 539.0 (4.41), 408.0 (5.38). Found, %: C 76.1; H 8.15; N 6.0. $C_{60}H_{76}Al \cdot ClN_4O_2$. Calculated, %: C 76.04; H 8.08; Al 2.85; Cl 3.74; N 5.91; O 3.38.

ACKNOWLEDGMENTS

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