ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 8, pp. 1548–1555. © Pleiades Publishing, Ltd., 2013.
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The State and Stability of Magnesium(II) Complexes with Azaporphyrins in the Proton-Donor Medium

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Received July 16, 2012

Abstract—The state and stability of magnesium complexes with various azaporphyrins in the proton-donor media containing acetic acid have been studied. Kinetic parameters of the complexes dissociation have been determined, possible reactions mechanisms have been proposed.

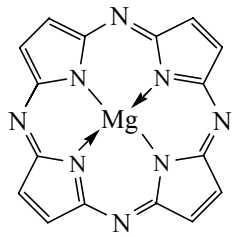
DOI: 10.1134/S1070363213080136

Chemical stabilization of azaporphyrins metal complexes is affected by the metal ion nature, ligand structure, nature of the proton-donor medium, and the complex state under the conditions of the experiment. In its complexes, magnesium forms $3s3p^3 3d^2$-hybrid coordination bonds with nitrogen coordination centers, thus the complex is stabilized [1]. The MgN_4 group is planar. For example, the literature data [2] show that chlorophyll is a relatively stable complex with Mg–N coordination bonds of quite high degree of the covalent character. Magnesium complexes of azaporphyrins are bases containing electron donor centers (*meso*-nitrogen atoms) that are capable of involvement into acid-base interaction in a proton-donor medium, depending on the medium acidity. The complex stability will depend on its form, neutral or acidic, dominating under given conditions.

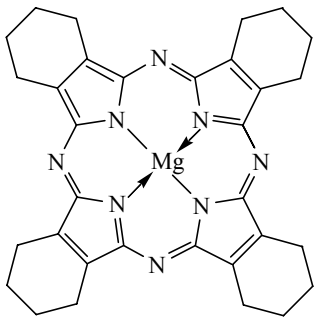
We studied the ligand structure effect on the state and stability of magnesium complexes with a series of azaporphyrins (H_2AP): 5,10,15,20-tetraazaporphyrin (H_2TAP), tetra(tetramethylene)tetraazaporphyrin ($H_2TTMTAP$), 5,7-diphenyl-1,4-diazeponitribenzoporphyrazine ($H_2Dz{\cdot}Bz_3Pz$), triazatetrabenzoporphyrin (H_2TATBP), and monoazatetrabenzoporphyrin (H_2MATBP) in the proton-donor media containing acetic acid.

The true (or, at constant medium acidity, effective) rate constant of the complex dissociation with the ligand elimination was taken as a measure of the complex stability. The complexes dissociation was followed at different temperatures: 30, 40, 50, and 60°C.

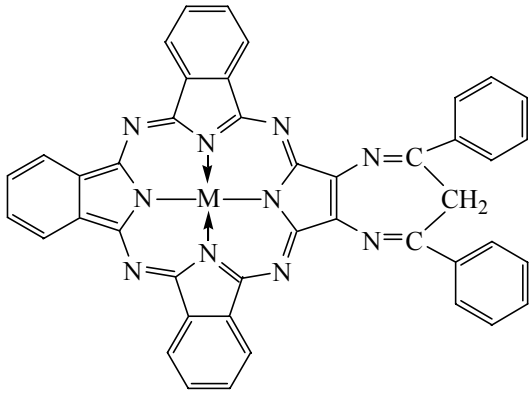
The stability of MgTAP, MgTTMTAP, and MgTATBP complexes was studied in the mixture of benzene and acetic acid with addition of ethanol (4%).



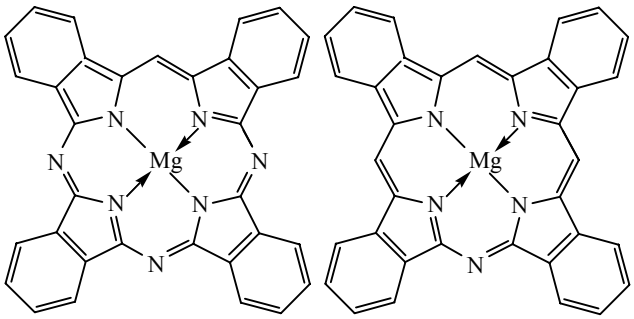
MgTAP



MgTTMTAP



$MgDzBz_3Pz$



MgTATBP MgMATBP

The complexes dissociation occurred with the formation of the respective free ligand in the non-protonated form.

$$MgAP + 2H^+ \rightarrow H_2AP + Mg^{2+}. \quad (1)$$

Figure 1 illustrates the changes of the complex electron absorption spectrum upon dissociation, MgTAP being a representative example. As acetic acid was taken in large excess with respect to the complex, the reaction was performed under conditions of the pseudo-first order reaction. The first order with respect to the studied complexes was confirmed by the linear shape of the log $(c^0_{MgAP}/c_{MgAP}) = f(\tau)$ plots (c^0 and c are initial and current concentrations of the complex, respectively, τ is the reaction time) (Fig. 2). Thus, the reaction was described by the first order kinetic equation (2) with k_{ef} being the effective rate constant of the complex dissociation.

$$-dc_{MgAP}/d\tau = k_{ef}c_{MgAP}. \quad (2)$$

Kinetic parameters of the studied reactions calculated on the basis of experimental data are collected in Tables 1–3. As seen from the tables, the dissociation rate constants were dependent on the acetic acid concentration. To determine the reaction order with respect to acetic acid, the $\ln k_{ef} = f[\ln c(CH_3COOH)]$ plots were analyzed. In the benzene–acetic acid–ethanol system at ethanol content below 4% the equilibrium (3) was established [1], and CH_3COOH concentration was proportional to square of $C_2H_5OH_2^+$ concentration.

$$CH_3COOH + C_2H_5OH \rightleftarrows C_2H_5OH_2^+ + CH_3COO^-. \quad (3)$$

Linear shape of the $\ln k_{ef} = f[\ln c(CH_3COOH)]$ dependence suggested that the dissociation of MgTAP, MgTTMTAP, and MgTATBP was induced by $C_2H_5OH_2^+$, thus being a solvoprotolytic dissociation [2]. The slope of those dependences was ~1 (Fig. 3), so the reaction was of the second order with respect to the solvated proton, and thus it proceeded according to the trimolecular mechanism developed in [3].

The kinetic equation of the complexes dissociation was as follows Eq. (4).

$$-dc_{MgAP}/d\tau = k_v c_{MgAP} c^2(C_2H_5OH_2^+). \quad (4)$$

The experimental data revealed that the most stable complex was MgTATBP. Such substitution stabilized the complex likely due to increased rigidity and aromaticity of the macrocycle [3].

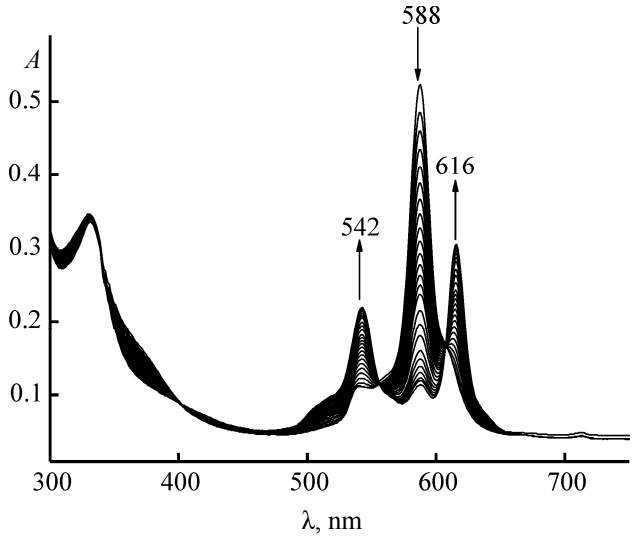


Fig. 1. Change in the electron absorption spectrum of MgTAP upon complex dissociation in the benzene – acetic acid – ethanol medium [$c(CH_3COOH)$ = 3.50 M, 323 K].

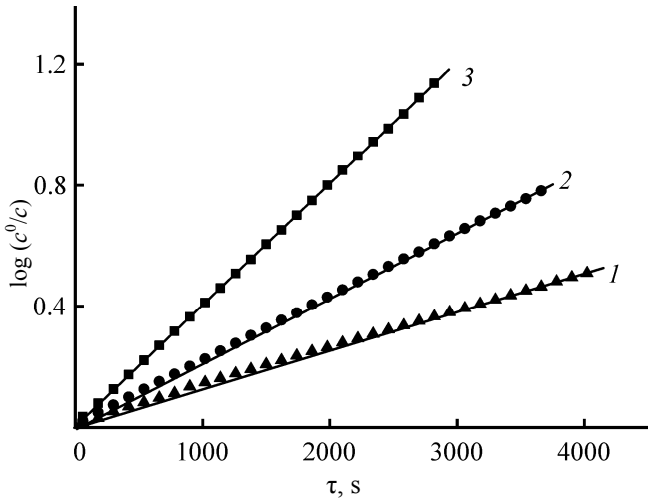


Fig. 2. log (c^0/c) as a function of time during MgTAP complex dissociation in the benzene–acetic acid–ethanol medium [$c(CH_3COOH)$ = 3.50 M]. (*1*) 303 K, (*2*) 313 K, and (*3*) 323 K.

Table 1. Kinetic parameters of MgTAP dissociation in the benzene–acetic acid–ethanol medium ($c^0_{MgTAP} = 5.76\times10^{-6}$ M)

$c(CH_3COOH)$, M	T, K	$k_{ef}\times10^3$, s^{-1}	E, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
0.87	298	0.02±0.01[a]	47±4	–185±6
	303	0.05±0.01		
	313	0.09±0.01		
	323	0.16±0.02		
1.75	298	0.04±0.03[a]	52±2	–163±4
	303	0.11±0.03		
	313	0.21±0.02		
	323	0.40±0.01		
2.62	298	0.07±0.03[a]	49±3	–168±5
	303	0.19±0.02		
	313	0.34±0.04		
	323	0.63±0.01		
3.50	298	0.12±0.04[a]	46±5	–174±3
	303	0.30±0.01		
	313	0.50±0.02		
	323	0.93±0.04		
4.37	298	0.13±0.03[a]	50±2	–160±6
	303	0.35±0.02		
	313	0.68±0.01		
	323	1.20±0.03		

[a] Calculated according to Arrhenius equation.

MgTAP was somewhat more stable than MgTTMTAP, even though the electron donor tetramethylene groups should have increased the covalent character of Mg–N bonds and thus the complex stability. There is no structural information about H_2TMTAP or its complexes available in the literature; our data demonstrate that tetramethylene groups are likely located out of the macrocycle plane and can thus lead to the macrocycle distortion and the Mg complex destabilization.

The stability of MgTTMTAP complex was also studied in the benzene–acetic acid medium in the absence of ethanol. In this medium the complex existed in the protonated form. Its dissociation proceeded with the formation of the ligand in the non-protonated form.

The reaction was carried out in the large excess of acetic acid, under conditions of the pseudo-first order reaction, thus, kinetic equation (2) was applied. The respective kinetic parameters are listed in Table 4. In the nonpolar aprotic solvent the complex dissociation occurred due to interaction with acetic acid molecules, thus, it was the case of acidoprotolytic dissociation. It

Table 2. Kinetic parameters of MgTTMTAP dissociation in the benzene–acetic acid–ethanol medium ($c^0_{MgTTMTAP} = 8.44\times10^{-6}$ M)

$c(CH_3COOH)$, M	T, K	$k_{ef}\times10^3$, s^{-1}	E, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
0.87	298	0.11±0.02[a]	21±6	–260±10
	303	0.15±0.01		
	313	0.22±0.04		
	323	0.25±0.01		
1.045	298	0.12±0.01[a]	20±5	–261±12
	303	0.17±0.04		
	313	0.24±0.03		
	323	0.28±0.03		
1.31	298	0.13±0.08[a]	32±4	–225±10
	303	0.18±0.01		
	313	0.29±0.04		
	323	0.39±0.07		
1.485	298	0.17±0.03[a]	26±2	–238±9
	303	0.29±0.06		
	313	0.40±0.05		
	323	0.55±0.07		

[a] Calculated according to Arrhenius equation.

was revealed that the effective rate constant of MgTTMTAP dissociation was independent of the acetic acid concentration, and the slope of the linear plots $\ln k_{ef} = f[\ln c(CH_3COOH)]$ was zero. Such result has never been reported before.

The mechanism of the acidoprotolytic dissociation is as follows. In the first stage (fast) acetic acid protonated the *meso*-nitrogen atom. In the second stage (slow), the intramolecular proton transfer from the *meso*-nitrogen atom to the endocyclic nitrogen atom of the MgN_4 group and the rupture of one of the Mg–N bonds occurred. The subsequent attack of CH_3COOH molecule leads to the fast rupture of the second Mg–N and to the formation of the free ligand. CH_3COO^- anions coordinated to Mg cation.

$$[MgTTMTAPH^+]^-OOCCH_3$$

$$\xrightarrow{slow} [Mg^+HTTMTAP]^-OOCCH_3 + CH_3COOH$$

$$\xrightarrow{fast} H_2TTMTAP + Mg(CH_3COO)_2. \quad (5)$$

MgTTMTAP dissociation in the benzene–acetic acid medium was approximately twice as fast as in the presence of ethanol, because the axial coordination of alcohol molecules impeded the solvated proton attack due to steric hindrance. Moreover, the complexes

Table 3. Kinetic parameters of MgTATBP dissociation in the benzene–acetic acid–ethanol medium ($c^0_{MgTATBP}$ = 5.39×10^{-6} M)

$c(CH_3COOH)$, M	T, K	$k_{ef}\times10^3$, s^{-1}	E, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
0.87	298	0.15±0.01[a]	39±6	–254±
	313	0.31±0.04		
	323	0.57±0.04		
	333	0.77±0.02		
1.31	298	0.20±0.03[a]	42±6	–202±8
	313	0.41±0.02		
	323	0.83±0.03		
	333	1.10±0.04		
1.75	298	0.27±0.04[a]	48±2	–180±4
	313	0.69±0.03		
	323	1.20±0.03		
	333	2.10±0.04		
2.185	298	0.37±0.01[a]	44±1	–190±3
	313	0.87±0.02		
	323	1.50±0.05		
	333	2.40±0.04		
2.62	298	0.59±0.02[a]	43±5	–190±10
	313	1.30±0.02		
	323	2.50±0.04		
	333	3.50±0.05		

[a] Calculated according to Arrhenius equation.

protonation decreased their stability due to weakening of the Mg–N bonds.

In the benzene–acetic acid medium, the *meso*-nitrogen atom of $MgDzBz_3Pz$ was protonated [4]. The complex dissociation in this medium was acidoprotolytic as well, and proceeded with the formation of the non-protonated ligand (Fig. 4). The slope of linear plot $\ln k_{ef} = f[\ln c(CH_3COOH)]$ was ~1 (Fig. 5, Table 5). Thus, in the case of $MgDzBz_3Pz$ dissociation one molecule of acetic acid participated in the rate-limiting stage of the reaction.

We suggest the following scheme of $MgDzBz_3Pz$ dissociation [Eq. (6)].

$$[MgDzBz_3H^+_{meso}Pz]^-OOCCH_3$$

$$\downarrow \text{slowly}, +CH_3COOH$$

$$[Mg^+HDzBz_3H^+_{meso}Pz](^-OOCCH_3)_2$$

$$\downarrow \text{fast}, +CH_3COOH$$

$$H_2DzBz_3Pz + Mg(CH_3COO)_2 + CH_3COOH. \qquad (6)$$

Table 4. Kinetic parameters of MgTTMTAP dissociation in the benzene–acetic acid medium ($c^0_{MgTTMTAP} = 8.44\times10^{-6}$ M)

$c(CH_3COOH)$, M	T, K	$k_{ef}\times10^3$, s^{-1}	E, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
0.44	298	0.22±0.02[a]	48±2	–164±4
	303	0.56±0.02		
	313	1.02±0.01		
	323	1.81±0.03		
0.87	298	0.22±0.02[a]	50±4	–156±6
	303	0.56±0.03		
	313	1.10±0.02		
	323	1.92±0.03		
1.31	298	0.22±0.02[a]	50±1	–155±1
	303	0.57±0.02		
	313	1.12±0.02		
	323	2.00±0.04		
1.75	298	0.22±0.02[a]	50±2	–157±5
	303	0.58±0.03		
	313	1.11±0.03		
	323	2.02±0.02		

[a] Calculated according to Arrhenius equation.

The intramolecular proton transfer did not occur in the case of $MgDzBz_3Pz$, likely due to higher basicity of the *meso*-nitrogen atoms. To support this assumption, we have studied the state of $H_2TTMTAP$ in the CH_2Cl_2–CF_3COOH medium.

Figure 6 illustrates the spectral changes the during titration of the porphyrazine dissolved in dichloromethane with trifluoroacetic acid, CF_3COOH concentration being in the range of 3×10^{-4}–1.3×10^{-2} M.

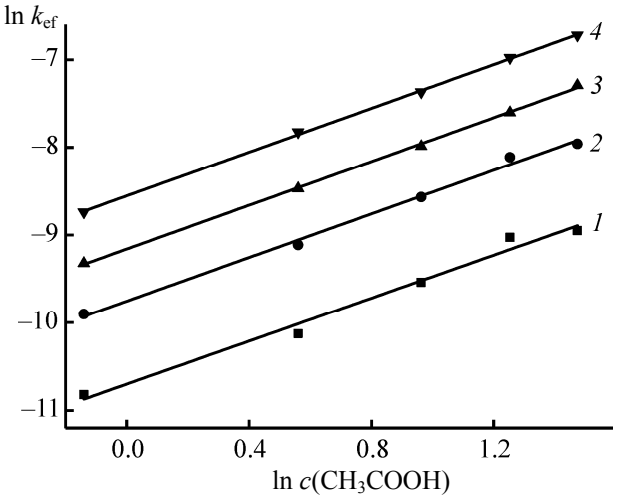


Fig. 3. Dependence of ln k_{ef} on ln $c(CH_3COOH)$ in the case of MgTAP dissociation at different temperatures: (*1*) 298 K, (*2*) 303 K, (*3*) 313 K, and (*4*) 323 K.

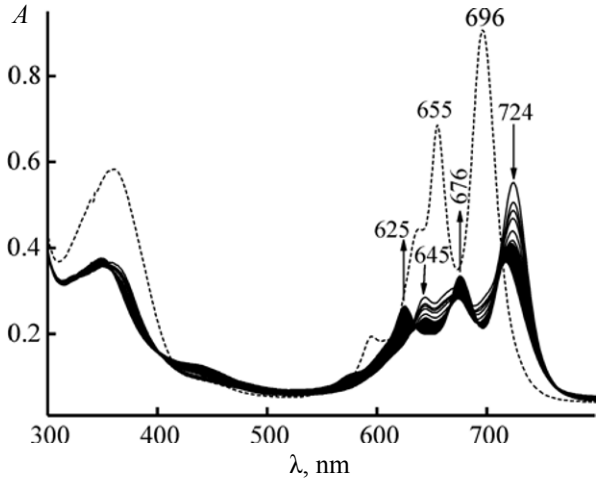


Fig. 4. Change in the electron absorption spectrum of $MgDzBz_3Pz$ upon complex dissociation, in the benzene–acetic acid–ethanol medium [$c(CH_3COOH)$ = 3.50 M, 323 K). (Dashed plot) shows the electron absorption spectrum of non-protonated $MgDzBz_3Pz$.

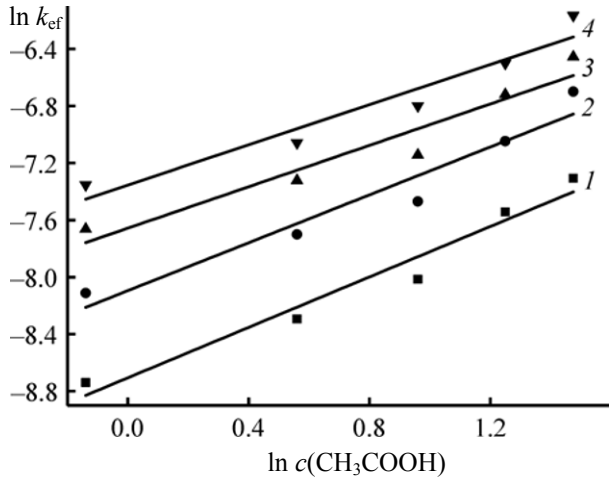


Fig. 5. Dependence of ln k_{ef} on ln $c(CH_3COOH)$ in the case of $MgDzBz_3Pz$ dissociation at different temperatures: (*1*) 298 K, (*2*) 303 K, (*3*) 313 K, and (*4*) 323 K.

The observed red shift of *Q*-band in the electron absorption spectrum of $H_2TTMTAP$ (624 → 643 nm and 557 → 568 nm) was characteristic of the protonation of *meso*-nitrogen atoms [5]. In order to determine the number of CF_3COOH involved in the acid-base interaction, we analyzed the log I_i = f[log $c(CF_3COOH)$] dependence (Fig. 7). The slope of this linear plot equaled 1.74. It is known that for the media containing trifluoroacetic acid the slope values above 1 can be due to homoconjugation effect, when trifluoroacetate ion is stabilized by association with one or several acid molecules: $=NH^+\cdots{}^-OOCCF_3$ $(HOOCCF_3)_n$, as well as due to specific features of the porphyrazine solvation. Thus, we could not estimate the number of donor centers participating in the acid-base interaction. The stability constant of acidic form (pK) as determined by spectrophotometric titration equaled 2.36±0.01.

Table 5. Kinetic parameters of $MgDzBz_3Pz$ dissociation in the benzene–acetic acid medium ($c^0_{MgDzBz3Pz}$ 7.13×10^{-6} M)

$c(CH_3COOH)$, M	T, K	$k_{ef}\times10^3$, s^{-1}	E, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
0.87	298	0.16±0.02[a]	33±2	–215±10
	313	0.30±0.01		
	323	0.47±0.04		
	333	0.64±0.01		
1.75	298	0.25±0.01[a]	21±3	–249±12
	313	0.53±0.04		
	323	0.66±0.03		
	333	0.86±0.03		
2.62	298	0.33±0.08[a]	22±4	–230±10
	303	0.57±0.01		
	313	0.79±0.04		
	323	0.99±0.07		
3.50	298	0.53±0.03[a]	22±3	–241±9
	303	0.87±0.06		
	313	1.21±0.05		
	323	1.50±0.07		
4.37	298	0.67±0.05[a]	26±2	–227±12
	303	1.10±0.03		
	313	1.57±0.04		
	323	2.10±0.08		

[a] Calculated according to Arrhenius equation.

H_2DzBz_3Pz protonation was studied earlier [4] and it was shown to occur in the trifluoroacetic acid concentration range of 0–0.04 M in the CH_2Cl_2–CF_3COOH medium; pK value being 2.45±0.06. However, in this case the diazepine nitrogen atom was protonated, leading to monoprotonated form, [H_2{DzH^+}Bz_3Pz].

$MgDzBz_3Pz$ protonation occurred via the *meso*-nitrogen atom in the CH_2Cl_2–CF_3COOH medium, at $c(CF_3COOH)$ = 0–1.3×10^{-2} M [4]. Thus, in the case of Mg complex, oppositely to the case of the free ligand, the basicity of the *meso*-nitrogen atoms of porphyrazine macrocycle was higher than that of the diazepine cycle, due to significantly ionic character of the complex. Unfortunately, the corresponding pK value could not be determined because its dissociation

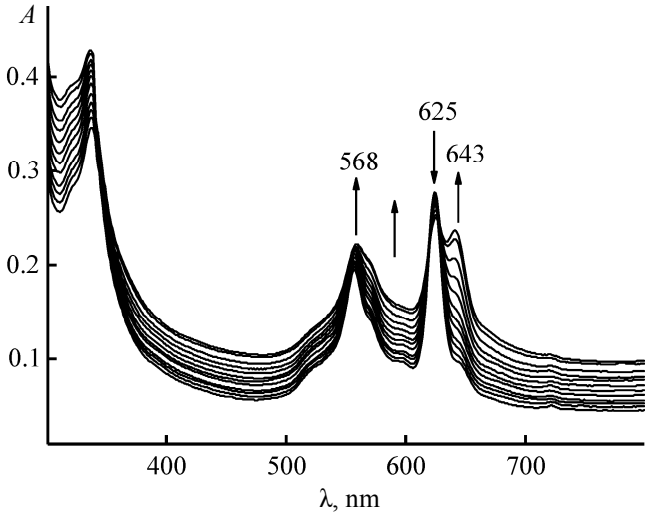


Fig. 6. Change in the H_2TTMTAP electron absorption spectrum upon acid-base interaction in the dichloromethane–trifluoroacetic acid medium.

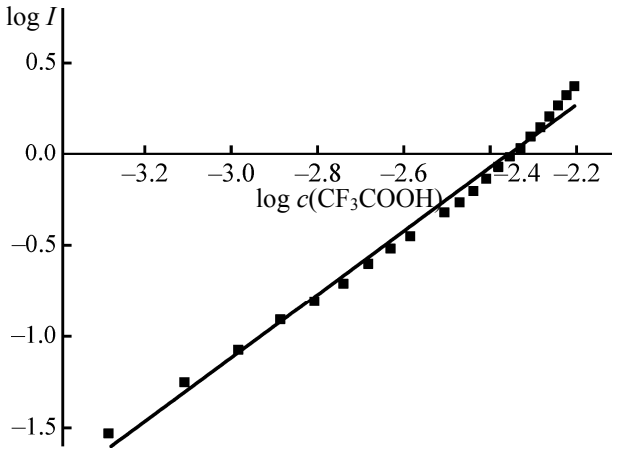


Fig. 7. log I = f[log c(CF_3COOH)] in the case of H_2TTMTAP acid-base interaction in the dichloromethane–trifluoroacetic acid medium.

proceeding simultaneously with protonation. As H_2DzBz_3Pz basicity was higher than that of H_2TTMTAP (due to the fusion of the benzene cycles with the macrocycle), the basicity of $MgDzBz_3Pz$ was, correspondingly, higher than that of MgTTMTAP.

MgMATBP was stable in the benzene–acetic acid medium and occurred in the form with the protonated *meso*-nitrogen atom. Fig. 8 illustrates the spectral changes observed upon addition of acetic acid to the benzene solution of MgMATBP at $c(CH_3COOH)$ = 1.75×10^{-6}–7.43×10^{-4} M: the decrease in the absorption of the bands at 647 and 63, and the increase in the absorption of the bands at 665 and 689 nm. Such shift of the *Q*-band is typical of the protonation of the porphyrazine macrocycle *meso*-nitrogen atom [5]. The appeared acidic form was preserved in the pure CH_3COOH. In order to determine the number of CH_3COOH molecules participating in the acid-base interaction, we analyzed the log I_i = f[log $c(CH_3COOH)$] dependence (Fig. 9). The slope of this linear plot was 1, which corresponded to a single donor center in MgMATBP molecule. The pK value of the acidic form, as determined by means of spectrophotometric titration, equaled +4.14±0.01. The significant basicity of MgMATBP was due to the substantial distortion of the macrocycle planar structure induced by *meso*-monoazasubstitution [6, 7], thus reducing the participation of the *meso*-nitrogen atom in the n,π-conjugation with the macrocycle. MgMATBP was stable in the pure trifluoroacetic acid as well. We suggest that benzosubstitution of the macrocycle stabilized the complex. In another study [8], the stability of Mg complex with triphenylmonoazatetrabenzoporphyrin in the benzene–acetic acid medium was investigated. It was shown that the complex was unstable and dissociated at $c(CH_3COOH)$ = 1.12–8.37 M. Probably, the three phenyl groups at the periphery of the molecule induced its distortion and thus destabilized the complex.

Thus, MgMATBP complex was the most stable in the benzene–acetic acid medium, despite of the macrocycle distortion: this complex was stable under conditions where the other complexes dissociated; the rate constants of other complexes dissociation were of the same order.

In [1], the macrocyclic effect was discussed as a tool for controlling the reactivity of tetrapyrrole macrocyclic compounds. The macrocyclic effect of porphyrins, azaporphyrins, porphyrazines, and their metal complexes is a phenomenon of atomic-electronic screening of the reactive sites H_2N_4 and MN_4. It alters the compound reactivity via the π-electronic and structural factors. The structural part of the macrocyclic effect is characterized by the extent of the atomic-electronic screening of the reactive sites of the molecule; its effect is enhanced with the increase of aromaticity. The electronic part is determined by the efficiency of the transmission of the effect of peripheral groups to the reactive sites. The kinetic stability of the Mg complexes studied in this work was

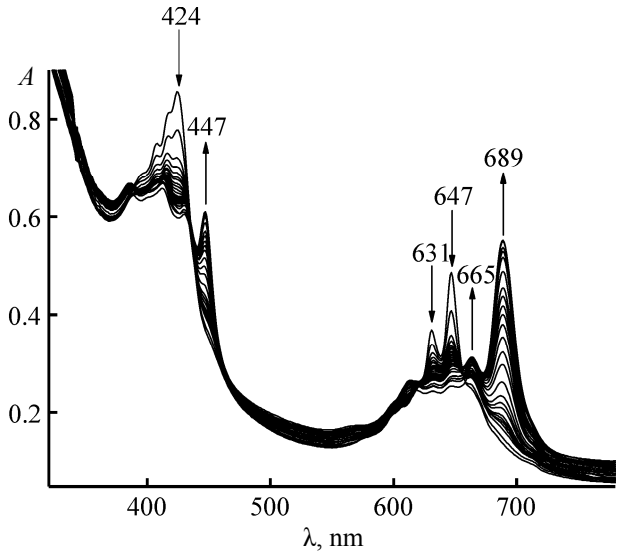


Fig. 8. Change in the MgMATBP electron absorption spectrum upon acid-base interaction in the benzene –acetic acid medium.

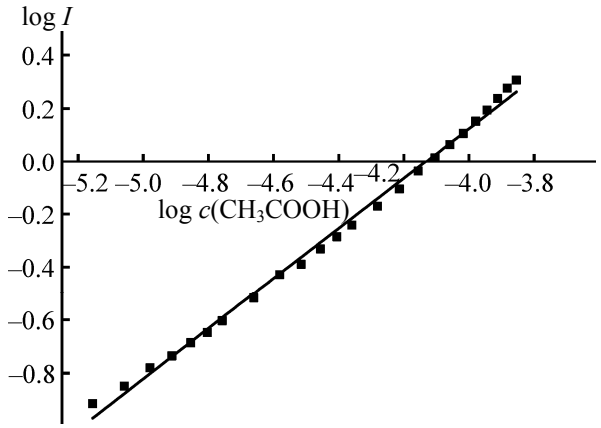


Fig. 9. log $I = f$[log c(CH_3COOH)] in the case of MgMATBP acid-base interaction in the benzene–acetic acid medium.

likely to be mainly due to the structural part of the macrocyclic effect and was due to the macrocycles aromaticity, while the effect of peripheral substituents was not that significant.

EXPERIMENTAL

Glacial acetic acid (chemically pure grade) was multiply freezed out and boiled with acetic anhydride. Then it was distilled (bp 118°C). Benzene was boiled at reflux above P_2O_5 for several hours and then distilled under atmospheric pressure, the intermediate fraction was collected (bp 80–81°C). Ethanol was boiled for 4 hours with calcined CaO, then CaO was separated, and ethanol was distilled (bp 78°C). Dichloromethane (chemically pure grade) was distilled under atmospheric pressure above monoethanolamine (bp 40°C).

Azaporphyrins complexes were prepared as described in [4, 9–11] and characterized by electron absorption spectroscopy and by elemental analysis.

Kinetic studies were performed in the temperature-controlled cell of Shimadzu UV-1800 photometer at varied temperature. The effective rate constant was calculated from the absorbance change at wavelengths corresponding to the bands maxima (588 nm in the case of MgTAP, 601 nm in the case of MgTTMTAP, 675 nm in the case of MgTATBP, and 645 nm in the case of $MgDzBz_3$) according to Eq. (7).

$$k_{ef} = 2.303/\tau[\log (A_0 - A_\infty)/A_\tau - A_\infty], \quad (7)$$

where A_0, A_τ, and A_∞ are initial, current and final solution absorbance, respectively.

For studies of acid-base interaction of MgMATBP and H_2TTMTAP, porphyrazines solutions of constant concentration were prepared in media with varied acidity, and the electronic absorption spectra were recorded with Shimadzu UV-1800 spectrophotometer at 298 K. The ratio of concentrations of acidic and basic forms at equilibrium ($I_i = c_i/c_{i-1}$) was determined from absorbance at wavelength corresponding to the acidic form absorption maximum.

The concentration stability constants of the conjugate acids in the benzene–CH_3COOH and dichloromethane–CF_3COOH media were calculated according to (8).

$$pK_i = \log I_i - n\log c[CH_3COOH(CF_3COOH)], \quad (8)$$

where $I_i = c_i/c_{i-1}$ is the ratio of ith and (i–1)th acidic forms concentrations in equilibrium (indicator ratio); n is the number of porphyrazine donor centers participating in the acid-base interaction in the respective stage.

MgTAP. Electron absorption spectrum (pyridine), λ, nm (log ε): 334 (4.60), 540 (4.14), 587 (5.07). Found, %:C 55.0; H 3.6; N 30.1. $C_{16}H_8MgN_8\cdot(CH_3OH)$. Calculated, %: C 55.4; H 3.3; N 30.4.

MgTTMTAP. Electron absorption spectrum (pyridine), λ, nm (log ε): 347 (5.00), 550 (4.26), 595

(5.12). Found, %: C 68.9; H 6.1; N 19.0. $C_{32}H_{32}MgN_8 \cdot (H_2O)$. Calculated, %: C 67.0; H 5.8; N 19.9.

$MgDzBz_3Pz$. Electron absorption spectrum (pyridine), λ, nm (log ε): 357 (4.78), 657 (4.76), 696 (4.82). Found, %: C 69.71; H 4.08; N 18.19. $C_{43}H_{24}MgN_{10} \cdot (H_2O)$. Calculated, %: C 69.69; H 3.81; N 18.90.

MgMATBP. Electron absorption spectrum (pyridine), λ, nm (log ε): 434 (5.02); 630; 644 (4.48). Found, %:C 75.89; H 3.40; N 12.18. $C_{35}H_{19}MgN_5$. Calculated, %: C 76.16; H 3.84; N 12.18.

MgTATBP. Electron absorption spectrum (pyridine), λ, nm (log ε): 653; 674 (5.11). Found, %: C 70.94; H 3.34; N 17.46. $C_{33}H_{17}MgN_7$. Calculated, %: C 73.97; H 3.20; N 18.30.

ACKNOWLEDGMENTS

This work was financially supported by the President of the Russian Federation (grant no. MK-4171.2012.3).

REFERENCES

1. Berezin, B.D., *Makrociklicheskii effekt i strukturnaya khimiya porfirinov* (Macrocyclic Effect and Structural Chemistry of Porphyrins), Moscow: Krasand, 2010.
2. Berezin, B.D. and Lomova, T.N., *Reaktsii dissociacii kompleksnykh soedinenii* (Reactions of Dissociation of Complex Compounds), Moscow: Nauka, 2007.
3. Berezin, B.D., *Koordinatsionnaya khimiya porfirinov i ftalocianina* (Coordination Chemistry of Porphyrins and Phthalocyanine), Moscow: Nauka, 1978.
4. Donzello, M.P., Ercolani, C., Mannina, L., Viola, E., Bubnova, A., Khelevina, O.G., and Stuzhin, P.A., *Austr. Chem.*, 2008, vol. 61, p. 262.
5. Leznoff, C.C., and Lever, A.B.P. (Eds.), *Phthalocyanines. Properties and Applications*, New York: VCH Publ., 1996, vol. 4.
6. Stuzhin, P.A., *J. Porph. Phthaloc.,* 2003, vol.7, no. 12, p. 813.
7. Das, J.M., and Chaudhuri, B., *Acta Cryst.*, 1972, vol. 28, p. 579.
8. Berezin, D.B. and Shukhto, O.V., *Proc. Univ. Ser. Chem. Chem. Technol.*, 2003, vol. 46, no. 8, p. 34.
9. Linstead, R.P. and Whalley, M., *J. Chem. Soc.,* 1952, p. 4839.
10. Brown, M., Spiera, P., and Whalley, M., *J. Chem. Soc.*, 1957, p. 2882.
11. Kachura, T.F., Mashenkov, V.A., Solov'ev, K.N., and Shkirman, S.F., *Vesti Akad. Nauk Bel. SSR, Ser. Khim*., 1969, no. 1, p. 65.