ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2007, Vol. 52, No. 3, pp. 394–397. © Pleiades Publishing, Inc., 2007.
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COORDINATION COMPOUNDS

Ligand Substitution Equilibrium in the Macrocyclic Molybdenum(V) Complex

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Received February 26, 2006

Abstract—The thermodynamics of the reaction of tetraphenylporphyrin(oxo)(hydroxo)molybdenum with imidazole (Im) in toluene was studied spectrophotometrically in a polythermal mode. It was established that the reaction of Im with O=Mo(OH)TPP includes several stages, two of which can be studied by spectrophotometrical titration. The first equilibrium stage is Im coordination to the eighth coordination site ($K_1 = 1.85 \times 10^3$ l/mol), the second stage is the coordination of the second Im molecule with the displacement of OH^- into the outer sphere ($K_2 = 4.80 \times 10^2$ l/mol). The enthalpy and entropy contributions to the stability constant of tetraphenylporphyrin molybdenum(V) complexes with Im were determined.

DOI: 10.1134/S0036023607030175

Metalloporphyrins possess a variety of useful properties owing to great possibilities of modifying their structure and the nature of central atoms. These properties are due to the reactivity of metalloporphyrins toward bases with a simpler structure than that of macrocyclic porphyrin ligand. The nature of the central atom in metalloporphyrins and the degree of its coordination saturation are significant factors [1]. The study of coordination of molecular ligands by coordinationally unsaturated metalloporphyrins is one line of in the chemistry of porphyrins. Extra coordination for mixed-ligand acido porphyrin complexes of metal cations in higher oxidation states, in particular for molybdenum(V) complexes [2, 3], is less studied. The O=Mo(OH)TPP complex studied in this work contains acido ligands in the coordination sphere in addition to the porphyrin macrocycle. In this complex acido ligands O^{2-} and OH^- are in the *trans* position to the plane of coordinated nitrogen atoms [4] and are tightly held in the coordination sphere [5]. The Mo–N bonds in O=Mo(OH)TPP are even more stable: the M–N bonds in this complex do not break even in superacids [5]. Therefore, the reactions with molecular ligands proceed for O=Mo(OH)TPP as the substitution reactions of acido ligands in the first coordination sphere along with extra coordination. This work deals with a quantitative study of the equilibria of reactions of tetraphenylporphyrin(oxo)(hydroxo)molybdenum with imidazole (Im) in toluene using electronic absorption spectroscopy and spectorophotometric titration.

EXPERIMENTAL

The O=Mo(OH)TPP complex was synthesized by complexing purchased porphyrin and molybdenum(VI) oxide using the procedure from work [6]: 0.1 g (0.16 mmol) of H_2TPP was boiled with 0.076 g (0.53 mmol) of MoO_3 in 0.8 g of phenol at 454 K for 4 h. The synthesis was finished, when the absorption bands of H_2TPP (λ_{max}, nm: 648.0, 592.0, 551.0, 516.0, 485.0, 420.0) disappeared from the electronic absorption spectrum of the reaction mixture. The complex was isolated in solid state by vacuum distillation of phenol. Then, a saturated solution of the complex in chloroform was prepared and purified to spectral purity by two-stage chromatography on Al_2O_3 using chloroform as solvent and eluent. The yield of the complex was 60%. The electronic absorption spectrum in chloroform (λ_{max}, nm ((log ε)): 620.0 (2.94), 584.0 (2.92), 456.0 (3.78)) corresponds to that measured in work [7]. The electronic absorption spectrum was recorded on SF-26 and Specord M-40 spectrophotometers.

The thermodynamics of the reaction of O=Mo(OH)TPP with Im in toluene was studied by spectrophotometric titration in a polythermal mode. The solutions of metalloporphyrin in toluene were prepared directly before the use. Optical density measurements for a series of solutions with $c_{O=Mo(OH)TPP}$ = const at various Im concentrations and T = 298–323K were carried out at a working wave length close to the maximum absorption band of the starting metalloporphyrin (465 nm). The accuracy of temperature control was ±0.1 K. The aforementioned series of working solutions was prepared by mixing calculated volumes of metalloporphyrin solution, Im solution in toluene with a known concentration, and pure toluene.

The equilibrium constants of O=Mo(OH)TPP reactions with Im producing new complexes $(Im)_m(X)_{m_1}$MoTPP (X is an acido ligand, $m = 0–3$, $m_1 =$

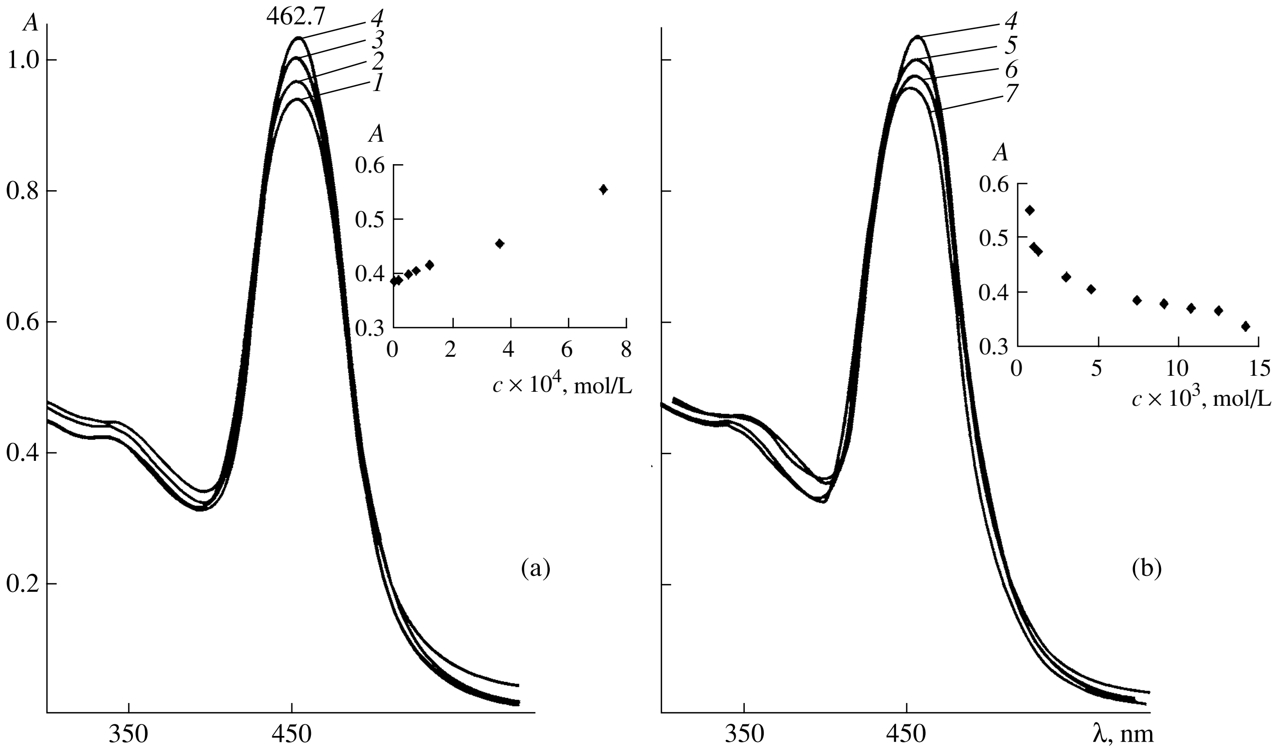

Fig. 1. Electronic absorption spectra of O=Mo(OH)TPP in toluene depending on Im concentration and the corresponding titration curves at the first (a) and second (b) stages. $c_{\mathrm{O=Mo(OH)TPP}} = 5.28 \times 10^{-6}$ mol/L; c_{Im}, mol/L: (*1*) 0, (*7*) 1.41×10^{-2}, and (*2*–*6*) intermediate concentrations.

0–2) were determined for the three-component equilibrium system (1) using the equation (2):

$$\mathrm{O{=}Mo(OH)TPP} + m\mathrm{Im} \rightleftharpoons (\mathrm{Im})_m(\mathrm{X})_{m_1}\,\mathrm{MoTPP}, \quad (1)$$

$$K = \frac{\dfrac{A_{\mathrm{eq}} - A_{\mathrm{o}}}{A_\infty - A_{\mathrm{o}}}}{1 - \dfrac{A_{\mathrm{eq}} - A_{\mathrm{o}}}{A_\infty - A_{\mathrm{o}}}} \, \frac{1}{c_{\mathrm{L}} - c^{\mathrm{o}}_{\mathrm{MP}} \dfrac{A_{\mathrm{eq}} - A_{\mathrm{o}}}{A_\infty - A_{\mathrm{o}}}}, \quad (2)$$

Here, $c^{\mathrm{o}}_{\mathrm{MP}}$ and c_{L} are, respectively, starting concentrations of metalloporphyrin and extra ligand in toluene solution; and A_0, A_{eq}, and A_∞ are optical densities at the working wave length of metalloporphyrin solutions, equilibrium mixture with a given concentration of the ligand, and a solution of the extra complex, respectively. The numerical values of constants K were determined from Eq. (2) by the least-squares method using the MS Excel program. The relative error in K determination was not higher than 7%.

The thermodynamic parameters of reactions of O=Mo(OH)TPP with Im ((3)–(5)) were determined from the temperature dependence of K:

$$\Delta H = R \ln \frac{K_2}{K_1} \left(\frac{T_1 T_2}{T_1 - T_2} \right), \quad (3)$$

$$\Delta G = -RT \ln K, \quad (4)$$

$$\Delta S = (\Delta H - \Delta G)/T. \quad (5)$$

The mathematical processing of the linear dependence –ln$K$ – 1/T. (6)

was carried out using the least-squares method and the MS Excel program.

$$-\ln K = \frac{\Delta H}{R}\frac{1}{T} - \frac{\Delta S}{R}. \quad (6)$$

RESULTS AND DISCUSSION

The reaction of O=Mo(OH)TPP with Im in toluene was studied spectrophotometrically in a wide range of Im concentrations from $1.20 \times 10^{-5} - 1.42 \times 10^{-2}$mol/l at 298–323 K. The upper limit of the Im concentration is determined by its solubility in toluene. According to the spectrophotometrical data and the titration curves (Fig. 1), the reaction includes two equilibrium stages. The electronic absorption spectrum of O=Mo(OH)TPP in toluene without Im (Fig. 1a, spectrum *1*) is a curve with a peak at 462.7 nm. At the first stage of the equilibrium process at low Im concentrations, an increase in the Im proportion brings about an insignificant increase in optical density at the wave length of the absorption maximum (spectra *2*–*4*), and an isosbestic point at λ = 459 nm is observed.

It was established experimentally that at low Im concentrations (1.20×10^{-5} to 7.18×10^{-4} mol/L), the equilibrium is achieved immediately after pouring the

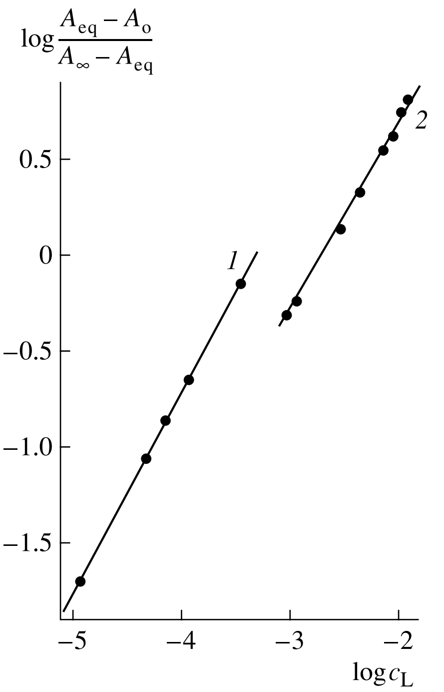

Fig. 2. Function $\log\dfrac{A_{eq} - A_o}{A_\infty - A_{eq}} - \log c_L$ for the reaction of O=Mo(OH)TPP with Im in toluene at the first (*1*) and second (*2*) stages (ρ = 0.999 and 0.998, respectively).

solutions together. The equilibrium constant K_1 at 298 K is $(1.85 \pm 0.11) \times 10^3$ L/mol. During the treatment of the relation in coordinates $\log\dfrac{A_{eq} - A_o}{A_\infty - A_{eq}} - \log c_L$, the number of Im molecules added at the first stage was found to be equal to one ($n_1 = 1.05$) (Fig. 2). The stoichiometry O=Mo(OH)TPP : Im = 1 : 1 and the spectral parameters permit us to write down the equation

$$\mathrm{O{=}Mo(OH)TPP + Im \xrightleftharpoons{K_1} O{=}Mo(OH)(Im)TPP}. \quad (7)$$

for the first stage of the reaction. This equation describes the extra coordination of the Im molecule by metalloporphyrin.

Stepwise equilibrium constants K_1 and K_2 of the reaction of O=Mo(OH)TPP with Im in toluene at various temperatures (working wave length, 465 nm)

T, K	$K_1 \times 10^{-2}$, L/mol	$K_2 \times 10^{-2}$, L/mol
298	18.5 ± 1.4	4.8 ± 0.2
303	16.3 ± 0.6	5.0 ± 0.3
308	14.1 ± 0.5	5.3 ± 0.2
313	11.6 ± 1.0	5.6 ± 0.2
318	9.2 ± 0.6	5.9 ± 0.3
323	8.1 ± 0.2	6.3 ± 0.3

The second equilibrium stage of the reaction of O=Mo(OH)TPP with Im in toluene takes place at Im concentrations from 7.18×10^{-4} to 1.42×10^{-2} mol/L. The equilibrium constant is $K_2 = (4.80 \pm 0.23) \times 10^2$ L/mol. As the Im concentration increases in this range, we observe a decrease in the intensity of the band at 462.7 nm and a small shift of the peak of this band to 460.5 nm (Fig. 1b, spectra *4–7*) with the conservation of the isosbestic point at λ = 461 nm, which points to more significant changes in the structure of the coordination sphere of metalloporphyrin compared to the first stage. After the titration data were treated as described for the first stage, one can assume in view of the data of Fig. 1b that the reaction of O=Mo(OH)TPP with Im at the second stage is the substitution of neutral Im for the single-charge OH^- ligand; OH^- is displaced to the outer sphere, and the cationic complex is formed:

$$\begin{gathered}\mathrm{O{=}Mo(OH)(Im)TPP + Im \xrightleftharpoons{K_1}} \\ \mathrm{[O{=}Mo(Im)_2TPP]^+ \cdot OH^-}.\end{gathered} \quad (8)$$

The stoichiometry of reaction (8) is confirmed by the treatment of $\log\dfrac{A_{eq} - A_o}{A_\infty - A_{eq}} - \log c_L$ ($n_2 = 1.00$) (Fig. 2).

At Im concentrations higher than 1.42×10^{-2} mol/L, we managed to study the spectra of the reaction mixtures just after their preparation. Imidazole precipitates with time in stored solutions, and spectrophotometric titration of the complex with Im solution becomes impossible. The band with the absorption peak at 460.5 nm hypsochromically shifts to 458.5 nm. Most likely, the Mo=O double bond is broken, and a cationic complex with a more intricate composition is formed.

A comparison of the equilibrium constants K_1 and K_2 shows that the presence of one Im molecule in the coordination sphere of the molybdenum(V) porphyrin complex hinders the coordination at the second stage of the process. The OH^- displacement from the coordination sphere in complex O=Mo(OH)(Im)TPP proceeds in time; equilibrium (8) is established within 15 min.

The table displays the equilibrium constants K_1 and K_2 at various temperatures.

The equilibrium constants K_1 and K_2 are linear functions of temperature (ρ is 0.994 and 0.997, respectively), which allows one to determine the thermodynamic parameters of reaction of O=Mo(OH)TPP with Im for both stages. The thermodynamic parameters are in accordance with the suggested scheme of stepwise reactions (7) and (8). At the first stage, the reaction is an exothermic process ($\Delta H_1^0 = -27.6 \pm 1.5$ kJ/mol) with a low negative value of ΔS^0 ($\Delta S_1^0 = -29.8 \pm 5.0$ J/(mol K)). The second stage is endothermic ($\Delta H_2^0 = 8.9 \pm 0.4$ kJ/mol) and has a greater positive value of ΔS^0 ($\Delta S_2^0 = 81.0 \pm 1.2$ J/(mol K)). The endothermic character of the second stage (Eq. (8)) points to the energy-consuming bond rupture in the reacting molecule O=Mo(OH)(Im)TPP, and the greater positive value of ΔS^0 points to the formation of less solvated species than the starting compounds. Indeed, the ionic associate $[O{=}Mo(Im)_2TPP]^+ \cdot OH^-$ is a self-solvated species and is poorly solvated by the solvent molecules, while the reagents for reaction (8) must be desolvated. The combination of the two factors leads to the disordering of the system and the increase in its entropy. The first stage of the reaction produces a neutral polar species, as the starting complex. Therefore, the slight decrease in the entropy of the system in the course of reaction (7) can be explained by a mere decrease of the number of species.

A comparative analysis of the data for the reactions of O=Mo(OH)TPP with various bases shows the following. The equilibrium of the reactions O=Mo(OH)TPP with Py, Im, and H_2S is characterized by a decreasing equilibrium constant, which is 9100 [8], 480, and 83 [9] L/mol, respectively. The products of the reaction with Py or H_2S, ($[O{=}Mo(Py)TPP]^+$ or O=Mo(SH)TPP) are characterized by the same coordination number, which corresponds to the increase in the protonation energy E from 438 [10] to 520 kJ/mol (calculated by the PM3 method by S.V.Zaitseva). The protonation energy means the energy amount absorbed upon the addition of one proton to the molecule of an organic base in vacuum. From this, the stability of axial ligands in complexes changes in accordance with the increase in the strength of the molybdenum–donor atom σ bond of the extra ligand. Among the studied bases, Im has the minimum E value (398 kJ/mol [10]). The equilibrium constant of the substitution of Im for OH^- does not correspond to the general tendency, which can be explained by the presence of an extra Im molecule in the complex $[O{=}Mo(Im)_2TPP]^+$. This Im molecule is coordinated at the previous stage.

In complexes containing Im, the coordination number achieves the highest value (eight) for the heavy transition metals. For octacoordinated complexes with noncyclic ligands, several geometric configurations exist. These complexes do not significantly differ in their stability, which makes them stereochemically nonrigid [11]. It is evident that in the case of porphyrin complexes, the reaction with Im yields rigid octacoordinated complexes O=Mo(OH)(Im)TPP and $[O{=}Mo(Im)_2TPP]^+$ with comparatively high stability constants for the imidazole ligand. These constants differ fourfold. The presence of stable stereochemical configurations can be expected for the complexes whose rigidity is due to the presence of an aromatic macrocycle in their composition. Unfortunately, other data on the geometry of the coordination spheres in the complexes are absent: mixed-ligand Im molybdenum complexes were obtained only in solution in contrast to the pyridine complexes studied in works [8, 12–14]; the latter can be easily prepared in solid state from metalloporphyrin solutions in 100% pyridine through pyridine evaporation.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no. 06-03-96343-r) and Program no. 8 of the Russian Academy of Sciences "Synthesis of Compounds with Designed Properties and Design of Functional Materials."

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