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Chromium(III) and Chromium(IV) Tetraphenylporphine Complexes

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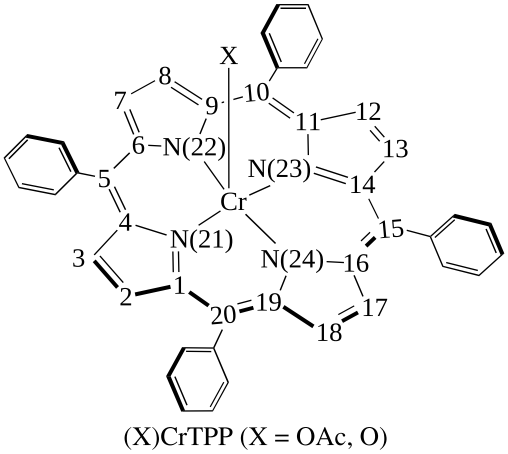
Abstract—Stable chromium complex (AcO)CrTPP was synthesized through the reaction of *meso*-tetraphenylporphine with chromium(III) acetate in boiling phenol. Coordination properties of chromium porphyrin in reaction with imidazole and pyridine in *o*-xylene were studied by electronic absorption spectroscopy and computer modeling. A single-electron oxidation of chromium(III) complex was found to be affected by peroxide compounds. The stability of an extra complex depends on the basic properties of the extra ligand and oxidation number of the central metal atom. The complex stability correlates with the calculated energy of formation of the metal–extra ligand bond. The geometrical structure and energy parameters of hexacoordinated chromium porphyrins were calculated using the quantum-chemical method. The effect of the *cis* and *trans* position of ligands in the composition of a macrocyclic compound was established to be significant only in the extra complexes (AcO)CrTPP.

The interest shown in porphyrins with high-valent metal cations is explained by the possibility of using them as efficient catalysts in redox processes and as initiators in radical polymerization reactions [1–4]. The d^2sp^3-hybridization of a metal atom in a porphyrin complex makes acidoligands X act as σ- and π-electron donors, which leads to the formation of stable complexes capable of reacting with the nitrogen-containing bases. However, such processes, in particular, for complexes with high-valent metal cations, have been poorly studied.

This work continues the systematic study of coordination properties of chromium porphyrins. The synthesis of (AcO)CrTPP (**I**), the single-electron oxidation of Cr(III) to Cr(IV) by peroxide compounds, and the mechanism of the extra coordination of chromium(III) and chromium(IV) tetraphenylporphine ((AcO)CrTPP, O=CrTPP) by imidazole (Im) and pyridine (Py), respectively, are considered.



(X)CrTPP (X = OAc, O)

EXPERIMENTAL

The reaction (AcO)CrTPP + *n*L = (AcO)Cr(L)$_n$TPP (L = Im, Py) was carried out in freshly prepared *o*-xylene (special purity grade) dried with metallic sodium [5]; *o*-xylene was used due to its relatively low reactivity.

Synthesis of (AcO)CrTPP. H_2TPP (0.1 g, 0.16 mmol) was boiled with chromium(III) acetate (0.2 g, 0.87 mmol) in phenol for 6 h. The extent of the reaction was monitored spectrophotometrically. The reaction mixture was cooled, dissolved in chloroform, repeatedly washed with warm water, and placed on a column with Al_2O_3. A dry complex was obtained after repeated chromatography and vacuum removal of $CHCl_3$. The yield was 50%. The compound was identified through elemental analysis, as well as electronic and ^{1}H NMR spectroscopies.

For $C_{46}H_{31}CrN_4O_2$			
anal. calcd. (%):	C 73.93;	H 6.48;	N 7.84.
Found (%):	C 74.02;	H 6.55;	N 7.70.

The electronic absorption spectra of the complex in chloroform (λ_{max}, nm (logε)): 605 (3.90), 565 (3.99), 523 (3.65), 450 (5.20), 396 (4.34), 358 (4.18); in acetic acid: 602 (3.99), 564 (4.12), 525 (3.70), 448 (5.31), 397 (4.61), 363 (4.40), which correspond to the literature data [6]; and in *o*-xylene: 604 (3.89), 564 (3.95), 525 (3.69), 448 (5.22), 398 (4.40), 365 (4.23).

^{1}H NMR in $CDCl_3$ (δ, ppm): 1.78 (m, *o*-H), 1.26 (m, *p*-H), 0.88 (t, CH_3).

The metalloporphyrin solutions in *o*-xylene were prepared just before they were used. The optical density

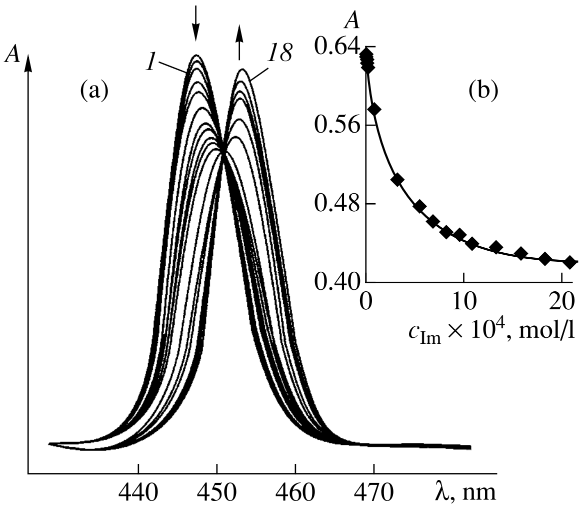


Fig. 1. (a) (*1–18*) Electronic absorption spectra of (AcO)CrTPP in *o*-xylene in the presence of imidazole with c_{Im} changing from 0 to 2.07×10^{-3} mol/l, $c^0_{(AcO)CrTPP} = 0.48 \times 10^{-5}$ mol/l and (b) the respective titration curve at λ = 445 nm.

of the studied solutions with different concentrations of Im and Py was measured at λ = 445 and 455 nm for (AcO)CrTPP and at λ = 432 and 544 nm for O=CrTPP, respectively.

The experimental procedure and the calculation of stability constants (K_{st}) of the extra complexes are described in [7–10]. For the ternary equilibrium system, K_{st} of the (X)Cr(L)TPP extra complexes (X = OAc, O; L = Im, Py) was calculated as

$$K_{st} = \frac{(A_s - A_0)/(A_\infty - A_0)}{1 - (A - A_0)/(A_\infty - A_0)} \times \frac{1}{(c_L - c^0_{MP})(A_s - A_0)/(A_\infty - A_0)},$$

where c^0_{MP} is the initial metalloporphyrin (MP) concentration in a solution, A_s is the optical density of an equilibrium solution, A_0 is the optical density of the MP solution, and A_∞ is the optical density of an equilibrium solution with the maximum extra ligand concentration. The relative error of the K_{st} determination did not exceed 10%.

Although the electronic absorption spectra of the extra complexes retain an isobestic point, which suggests that the solution under study contains two colored compounds, metalloporphyrins with one and two extra ligands have very similar electronic absorption spectra. A shift of the isobestic point is commensurable with the experimental error, and, therefore, the number of added ligands was determined by the Bent–French method [7].

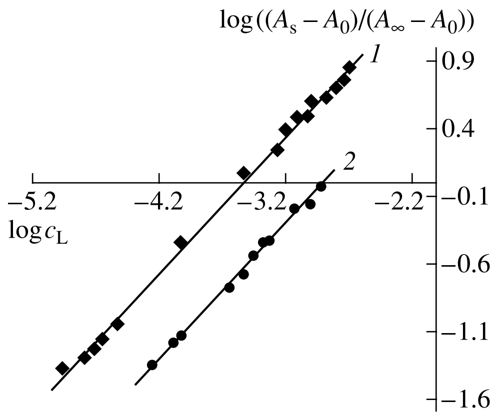


Fig. 2. Plots of $\log(A_s - A_0)/(A_\infty - A_0)$ vs. $\log c_L$ for extra coordination of (AcO)CrTPP with (*1*) Im and (*2*) Py.

Quantum-chemical calculations were performed by using both the Fletcher–Reeves and the Polak–Raivier methods [11–14].

The electronic absorption spectra were recorded using SF-26 and Specord M-400 spectrophotometers; ^{1}H NMR spectra were taken on a Bruker AC-500 spectrophotometer (500 MHz, HMDS as internal standard) in $CDCl_3$.

RESULTS AND DISCUSSION

The formation of the Cr–L σ-bond in the extra complex of chromium porphine results in a decrease in the effective positive charge on the chromium atom. Therefore, one could expect an increase in the energy of the $a_{1u}(\pi), a_{2u}(\pi) \longrightarrow e_g(d_\pi)$ transition. However, the reverse situation is observed. The introduction of extra ligand L into the metalloporphyrin solution and the further increase in the ligand concentration causes a bathochromic shift (Δλ) of the absorption bands in the electronic absorption spectra of the complex (Fig. 1a). This occurs due to the formation of a dative Cr–L π-bond that diminishes the electron density on the d_{xz} and d_{yz} orbitals of Cr(III).

The destabilization of the energy levels of the ground and excited states of a metallophophyrin as a result of extra coordination changes the configurational interaction and electronic structure of the chromophore. This causes a substantial shift and increase in the intensity of the main bands in the electronic absorption spectra of the extra complex. This spectral feature of the reaction of the extra coordination of Im and Py by chromium porphyrins makes it possible to use the spectrophotometric method in studies of mixed-ligand complexes.

Chromium porphyrins mainly occur in solutions as hexacoordinated compounds and, thus, one can suggest that in *o*-xylene the sixth coordination site of chromium is occupied by a water or solvent molecule. The (AcO)Cr(H_2O)TPP complex can form when the water

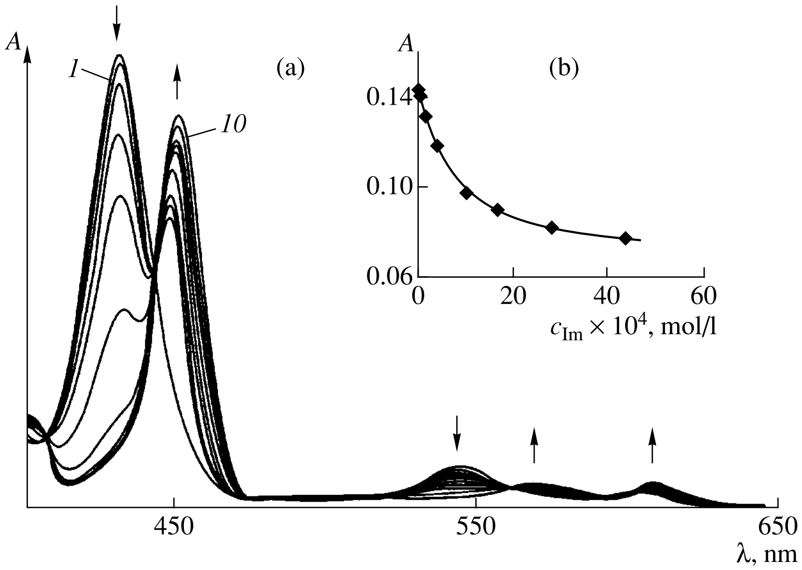


Fig. 3. (a) (*1–10*) Electronic absorption spectra of O=CrTPP in *o*-xylene in the presence of imidazole with c_{Im} changing from 0 to 4.36×10^{-3} mol/l, $c^0_{O=CrTPP} = 0.76 \times 10^{-5}$ mol/l and (b) the respective titration curve at λ = 544 nm.

concentration in a solvent does not exceed 10^{-3} mol/l [15, 16]. However, the content of H_2O in *o*-xylene dried with metallic sodium is about 10^{-7} mol/l, which is insufficient for H_2O coordination with metalloporphyrin. Note that $(CH_3)_2C_6H_4$ is "inactive" and poorly solvates the chromium atom [17]; the solvation mainly involves the peripheral part of a macrocyclic ligand. The energy of the Cr–$(CH_3)_2C_6H_4$ bond formation calculated by the ZINDO1 quantum-chemical method is equal to +37.47 kJ/mol, while that of the Cr–H_2O, Cr–Im, and Cr–Py bond is –116, –191.68, and –178.27 kJ/mol, respectively. This is why the energy spent on replacing a solvent molecule by a nitrous base is so insignificant and is commensurable with the measurement error. For this reason, we consider this process as a simple addition reaction of imidazole and pyridine when these occupy the sixth coordination site of the chromium atom.

On the basis of the results obtained, it was established that (AcO)CrTPP coordinates one molecule of Im or of Py ($\tan\alpha = 1.0$ and 0.99, respectively) (Fig. 2). This is clearly seen from the spectrophotometric titration curve of (AcO)CrTPP with imidazole (Fig. 1b). The monotonous nature of the curve is not violated, which suggests that the mixed-ligand complexes form in a one-stage reaction. The (AcO)CrTPP titration curve with pyridine is similar. After storage, the equilibrium systems did not change their electronic absorption spectra, which also confirms the common mechanism of the extra coordination process and the formation of a stable reaction product (AcO)Cr(L)TPP.

The stability constants of extra complexes of chromium(III) porphyrins were determined at 298 K in the concentration interval $c_{Im} = 1.5 \times 10^{-5}–2 \times 10^{-3}$, $c_{Py} = 2.7 \times 10^{-5}–3.2 \times 10^{-3}$ mol/l and are equal to 3.36×10^3 and 7.845×10^3 mol^{-1} l for (AcO)Cr(Im)TPP and (AcO)Cr(Py)TPP, respectively. When going from imidazole to pyridine, the Cr–L bond in the extra complex becomes weaker (Tables 1 and 2) due to the decrease in the basic properties of the extra ligand ($pK_{ImH^+} = 6.65$, $pK_{PyH^+} = 5.29$).

As is seen from the data in Table 1, the bathochromic shift Δλ is related to K_{st} of the extra complex. The value of Δλ can be used to qualitatively estimate the Cr–L bond strength and, hence, the displacement of the metal atom from the plane of the coordination center (N_4).

As was already noted above, the extra coordination reaction with chromium(III) porphyrins was conducted in *o*-xylene, which was washed with $Na_2S_2O_3$ and dried with metallic sodium according to the standard procedure [5]. In this solvent, the electronic absorption spec-

Table 1. Thermodynamic parameters of extra coordination of nitrogen-containing ligands to chromium porphyrins in *o*-xylene

Complex	$K^{298}_{st} \times 10^{-3}$, mol^{-1} l	$-E_b$, kJ/mol	Δλ, nm
(AcO)CrTPP			
(AcO)Cr(Im)TPP	3.36 ± 0.23	191.68	6
(AcO)Cr(Py)TPP	0.785 ± 0.028	178.27	4
O=CrTPP			
O=Cr(Im)TPP	1.75 ± 0.12	1.01	22
O=Cr(Py)TPP	0.258 ± 0.029	0.86	19

Table 2. Selected geometrical parameters of chromium porphyrins obtained by quantum-chemical calculations

Complex	Bond length, Å								
	Cr–N(21)	Cr–N(22)	Cr–N(23)	Cr–N(24)	Cr–N_L	Ct*–Cr	Cr–X	N(21)–N(23)	N(22)–N(24)
(AcO)CrTPP	2.1656	2.1654	2.1735	2.1734		0.5229	2.3913	4.2112	4.2110
(AcO)Cr(Im)TPP	2.0924	2.0962	2.0937	2.0984	2.1604	0.0456	2.2389	4.1852	4.1936
(AcO)Cr(Py)TPP	2.2283	2.1285	2.1118	2.1302	2.3051	0.0431	2.3926	4.3324	4.2578
O=CrTPP	2.1008	2.1007	2.1005	2.1004		0.5699	1.5867	4.0437	4.1225
O=Cr(Im)TPP	2.0996	2.1005	2.0998	2.1000	4.5746	0.5581	1.5871	4.0484	4.1239
O=Cr(Py)TPP	2.1006	2.1000	2.1006	2.0999	4.7636	0.5713	1.5869	4.0429	4.1221

* Ct is the center of a macrocycle plane.

trum of the (AcO)CrTPP complex contains a Soret band (*B*(0,0)) at λ_{max} = 448 nm due to the charge-transfer transition [18]. However, in the electronic absorption spectrum of the complex solution in *o*-xylene dried with NaOH [19] to the equilibrium content of water, 10^{-3} mol/l, this band was observed at 431.9 nm. The shift of the Soret band may occur due to the coordination of a water molecule and the formation of $(AcO)Cr(H_2O)TPP$.

Under the action of different oxidative agents, chromium(III) porphyrins are known to easily enter the redox reactions and form -yl complexes of Cr(IV) and Cr(V) [20–22]. Xylenes and toluene of reactive quality contain sufficient amount of organic peroxides to completely convert (AcO)CrTPP into O=CrTPP. The removal of a solvent with NaOH does not make it possible to eliminate the hydroperoxides it contains, and, thus, the oxidation of chromium(III) is more than probable. A single-electron oxidation under different conditions gives two products, namely, the π-cation-radical $(AcO)CrTPP^{\bullet+}$ or O=CrTPP [22]. In addition to maxima in the range of 400–550 nm, the first product contains absorption bands in the range of 600–840 nm, while the second product does not exhibit these bands in the long-wave region.

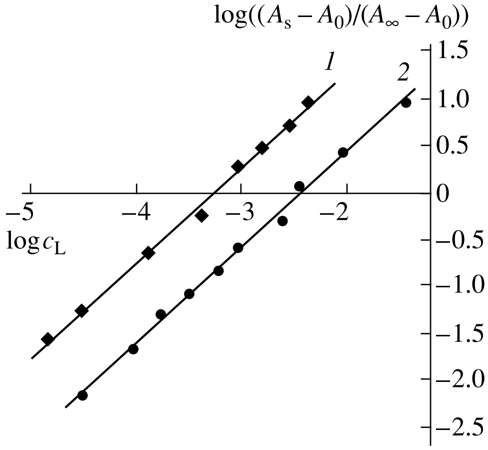


Fig. 4. Plots of $\log((A_s - A_0)/(A_\infty - A_0))$ vs. $\log c_L$ for extra coordination of O=CrTPP with (*1*) Im and (*2*) Py.

The electronic absorption spectrum of (AcO)CrTPP in *o*-xylene with a peroxide concentration 10^{-6}–10^{-5} mol/l contains bands with λ_{max} = 371.0, 431.9, 544.7, and 604.0 nm, which is typical of O=CrTPP [23–25].

As in the case of (AcO)CrTPP, O=CrTPP coordination with Im and Py molecules is accompanied by a bathochromic shift of the basic absorption bands (Fig. 3). However, the value of Δλ is considerably higher in this case (Table 1). Obviously, this is due to the fact that extra ligand coordination occurs simultaneously with the reduction of metalloporphyrins.

On the basis of the data obtained, it was established that O=CrTPP adds one molecule of Im or Py (tanα = 1.00 and 1.01, respectively) (Fig. 4). The titration curve (Fig. 3b), as with (AcO)CrTPP, falls smoothly maintaining its monotonous nature. The stability of the mixed-ligand complexes formed depends on the basicity of the extra ligands and decreases when going from imidazole to pyridine (Table 1). The stability constants of O=Cr(L)TPP are lower than those of the respective (AcO)Cr(L)TPP complexes (Table 1). We believe that the reason for this lies in that the covalently bonded π-donor acidoligand O^{2-} in O=CrTPP can significantly increase the electron density in the chromium *d* orbitals, which results in a decrease in its effective positive charge and, correspondingly, in the formation of a less stable Cr–N_L bond. The stability can also decrease due to steric factors, namely, due to the displacement of a metal from the N_4 plane (Table 2) and the reduction of chromium(IV) tetraphenylporphine occurring simultaneously with extra coordination.

The quantum-chemical calculations revealed that the metalloporphyrins under study have nonplanar structures with slightly raised and lowered (in pairs) pyrrole fragments (Fig. 5). The chromium atom is displaced from the N_4 plane toward the acidoligand (Table 2). The extra coordination of the Cr(III) complex is followed with substantial changes in the geometrical parameters of the coordination center of the porphyrin ligand (Table 2).

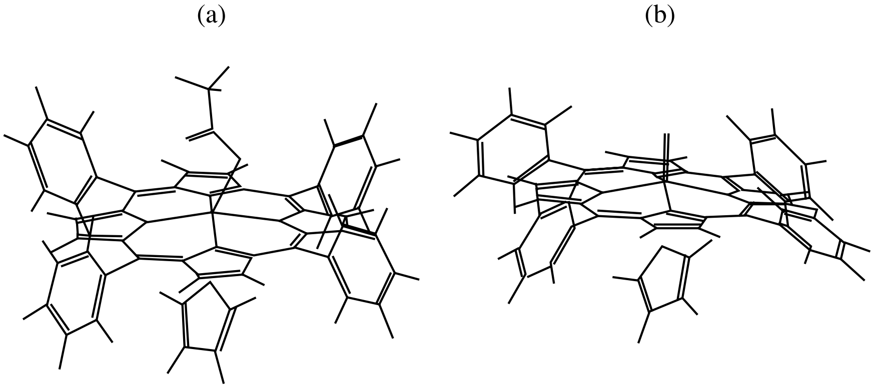


Fig. 5. Structures of (a) (AcO)Cr(Im)TPP and (b) O=Cr(Im)TPP calculated by the ZINDO1 quantum-chemical method.

The obtained data showed a correlation between K_{st} and the length of the Cr–N_L bond, whose strengthening increases the stability of the mixed-ligand complexes (Tables 1 and 2). It was established that the energy of formation of the M–L bond in a porphyrin complex changes symbatically with its stability (Table 1). At the same time, no correlation was found between the metal displacement from the N_4 plane and the Cr–N_L bond length (Table 2).

Analysis of the obtained geometrical parameters of the mixed-ligand compounds shows that the *trans* and *cis* effects of ligands in the Cr(III) and Cr(IV) complexes appear in different ways. A sufficiently strong *trans* effect of ligands is observed only in the case of (AcO)Cr(Im)TPP (Table 2). The *cis* effect is confirmed by the change in the M–N(21–24) bonds during the interaction of Cr(III) with the extra ligand molecule, while it is almost absent for Cr(IV) porphyrins (Table 2).

Thus, one can conclude that, unlike the (AcO)Cr(L)TPP complexes, the coordination of Im and Py to O=CrTPP does not cause significant distortions in a macrocycle.

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