ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 8, pp. 1563–1570. © Pleiades Publishing, Ltd., 2013.

Original Russian Text © T.N. Lomova, T.N. Sokolova, S.V. Zaitseva, S.A. Zdanovich, V.E. Maizlish, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 8, pp. 1334–1341.

Structure and Properties of Tetrakis[3(4)-chlorophthalocyaninato]copper(II) Protonated Forms in the Isolated State and in the Sulfuric Acid Solutions

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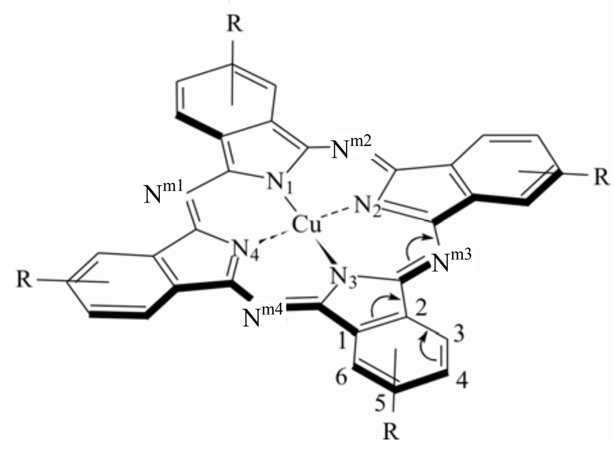
Received June 12, 2012

Abstract—Results of the quantum-chemical PM3 and experimental spectrophotometric studies of the stepwise protonation of tetrakis[3(4)-chlorophthalocyaninato]copper(II) are presented. The number, structure, and energy characteristics of consecutively protonated isolated molecules of the substituted complexes have been determined; the stability and electron absorption spectra of the complexes protonated forms in concentrated sulfuric acid solution have been studied. The special effect of substitution with halogen on the electronic structure of the exocyclic nitrogen atoms of (phthalocyaninato)copper(II) has been examined.

DOI: 10.1134/S107036321308015X

Many of the unique properties of phthalocyanines (H_2Pc) and their metal complexes (MPc) are due to delocalization of the macrocycle electrons. Symmetric or asymmetric substitution of the peripheral condensed benzene fragments is a convenient way to alter the electronic density of the macrocycle. In the case of symmetrical substitution, the electron density excess or deficit may be achieved; in the case of asymmetric substitution, the electronic structure becomes centrally asymmetric, and the push-pull effect is observed. Both approaches are widely applied in the experimental studies [1–6] as well as for technical applications in catalysis, thin-film optoelectronics, and nonlinear optics [7–10]. To efficiently utilize the substitution approach to H_2Pc and MPc structure modification, it is necessary to investigate the substituents effect on the electronic structure of these molecules.

Evidently, the direction of the electronic effects of substituents can change up to the opposite in going from one reaction site in the molecule to another and at the alteration of the reaction nature [11, 12]. We have recently studied the phthalocyanine substitution effects on the basicity, stability, and reactivity of MPc as a function of coordination interaction nature and the coordination center nature [4, 13–15]. Besides the coordination center, the exocyclic nitrogen atoms are MPc reactive sites, in particular, in reaction with protons. In this work we studied the stepwise protonation of chlorinated (phthalocyaninato)copper(II) $CuPc(R)_n$ (**I**, **II**) (both of isolated molecules and those in concentrated sulfuric acid medium) by means of computer simulation and spectrophotometry. With accounting for the previously obtained data on the



R = 3-Cl, $CuPc(3\text{-}Cl)_4$ (**I**); 4-Cl, $CuPc(4\text{-}Cl)_4$ (**II**); 3-NO_2, $CuPc(3\text{-}NO_2)_4$ (**III**); 4-NO_2, $CuPc(4\text{-}NO_2)_4$ (**IV**); (4-Br)·(5-NO_2), $CuPc(4\text{-}Br)(5\text{-}NO_2)_4$ (**V**).

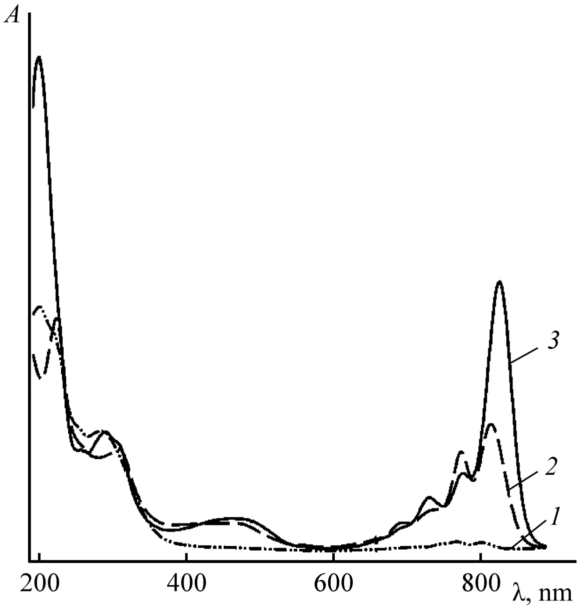


Fig. 1. Electron absorption spectra of the first (*1*), the second (*2*), and the third (*3*) protonated forms of CuPc(3-Cl)$_4$ in concentrated sulfuric acid.

stability of **I** and **II** [16] and for the known behavior of halonitro and nitro derivatives of CuPc (**III–V**) [17], the mechanism of the transfer of the chlorine substituent effect to the exocyclic nitrogen atoms was analyzed.

The investigation of MPc(R)$_n$ transformation in sulfuric acid solutions is a topical issue, as concentrated H_2SO_4 is practically the only solvent for phthalocyanines without additionally introduced solvation centers, not inducing Pc destruction. However, the quantitative parameters of the stepwise protonation of MPc(R)$_n$ in the sulfuric acid solutions have not been available due to the sharp decrease in the complexes solubility with H_2SO_4 dilution. Even in the case of tetrasulfo-substituted CuPc, characterized by enhanced solubility in the diluted H_2SO_4, the first protonation constant K_1 reported in the literature [18], corresponds to the associated complex form rather than to the isolated CuPc(SO$_3$H)$_4$. The protonation constants of MPc have been determined by the solubility method [19] under the condition of applicability of the Hammett equation, in the concentrated acid. Under these conditions, the indirect quantitative data like electron absorption spectra (EAS) of the individual protonated forms and their number are useful for the system characterization. In this work, such data were obtained by recording the electron absorption spectra of **I** and **II** and tracking their changes with variation of H_2SO_4 concentration in the range of true MPc solution existence (12–18 M). Under conditions of a single protonated form prevalence (indicated by the spectrum invariance with the acid concentration), the protonated forms spectra were recorded (Table 1). The PM3 optimization of the neutral and protonated CuPc(R)$_4$ molecules served as an independent method to track the substitution and protonation effects on the geometry, charge distribution on the atoms of CuPc, and the energy of the interaction with proton.

As seen from Table 1, the studied complexes acted as bases in the sulfuric acid medium. This was evidenced by the *Q*-bands red shift in the **I** and **II** electron absorption spectra, enhanced upon stepwise protonation; this red shift, being less pronounced, was similar to that observed upon single-electron oxidation of MPc [20]. In the latter case, due to electron elimination from the π-orbital, the electron transition within HOMO (π→π-transition) occurred, thus the intensive absorption appeared at the long-wave ramp of the B$_1$/B$_2$ bands. As no new bands appeared in the electron absorption spectrum upon protonation of CuPc(Cl)$_4$ (Fig. 1), it might be concluded that the interaction with protons was localized at the *n*-electron pairs of exocyclic nitrogen atoms, relatively isolated from the π-system. Unfortunately, for sparingly soluble CuPc(Cl)$_4$ it was not possible to directly observe the elimination of *n*→π*-transitions upon protonation (similarly to that observed in the case of carboxyl derivatives of CuPc as weak EAS bands at 540–575 nm in organic solvents [21]) as they were overlapped by the intensive *Q*-band.

According to the chosen parameter, the shift of band I upon protonation, the chlorine-containing complexes **I** and **II** were the most basic of the series of substituted complexes (Table 1), complex **I** being more basic than both complex **II** and non-substituted CuPc (observed $\Delta\lambda^{\mathrm{I}}_{\max}$ for the two protonated forms was 116 and 122 nm [17]). Additionally, this was supported by the formation of the third protonated form of complex **I**. The third protonated form was also observed in the case of 3-nitro derivative of CuPc apparently due to the contribution of steric effects to the basicity. This was clarified by the quantum-chemical simulation of MPc protonation processes, the corresponding results would be discussed below. The 4-substituted complexes showed similar relative basicities. Thus, the observed effects were similar to the electronic effects of the discussed groups in the electrophilic substitution reactions of benzene: NO$_2$ group, showing the –*I* and –*C* effects, decreased the complex basicity more than did the Cl group. However, the octa-substituted

Table 1. Electron absorption spectra bands λ_{max} of the substituted CuPc in pyridine and of its protonated forms in sulfuric acid, the relative I and II bands positions (λ^{I}_{max}, λ^{II}_{max}, nm), and the I band shift upon protonation ($\Delta\lambda^{I}_{max}$)

Complex	Pyridine[a]	H_2SO_4 [$c(H_2SO_4)$, M]	$\Delta\lambda^{I}_{max}$	λ^{I}_{max}–λ^{II}_{max}	
				Solv	H_2SO_4
The first protonated form					
$CuPc(3\text{-}Cl)_4$ (**I**)	676, 615^{c}	801, 766; 655^{c} (12.0)	125, 90	61	146, 111
$CuPc(4\text{-}Cl)_4$ (**II**)	674, 609^{c}	776, 747; 674^{c} (12.0)	102, 73	65	102, 73
$CuPc(3\text{-}NO_2)_4$ (**III**)[b]	669, 600^{c}	703; 628^{c} (12.0)	34	69	75
$CuPc(4\text{-}NO_2)_4$ (**IV**)[b]	669 675, 610^{d}	732, 701^{c}; 657^{c} (12.0)	57, 91^{d}	65^{d}	75, 44
$CuPc(4\text{-}Br)_4(5\text{-}NO_2)_4$ (**V**)[b]	680, 640^{d}	782, 757^{e}; 682 (17.0)	102, 117	40^{d}	100, 75
The second protonated form					
$CuPc(3\text{-}Cl)_4$ (**I**)	676, 615^{c}	813, 772; 726-746, 656^{c} (16.0)	139	61	87–67, 116
$CuPc(4\text{-}Cl)_4$ (**II**)	674, 609^{c}	799, 707; 655^{c} (17.0)	126.2	65	144, 52
$CuPc(3\text{-}NO_2)_4$ (**III**)	669, 600^{c}	719; 646 (15.9)	47	69	73
$CuPc(4\text{-}NO_2)_4$ (**IV**)	669 675, 610^{d}	753, 735; 660 (16.7)	91 98	65^{d}	93, 75
The third protonated form					
$CuPc(3\text{-}Cl)_4$ (**I**)	676, 615^{c}	825, 775^{c}; 729^{c} (17.7)	148.5	61	96, 46
$CuPc(3\text{-}NO_2)_4$ (**III**)	669, 600^{c}	728, 719^{c}; 645^{c} (17.7)	62.3	69	83

[a] Non-protonated form. [b] Data from [17]. [c] Shoulder. [d] In dimethylformamide, data of this work authors. [e] The *Q* band *Q* (743.7 nm) is referenced in [17], the shoulder at 782 nm is not referenced.

complex **V** was not the most basic, thus revealing that the impact of substituents effects on CuPc basicity was more complicated.

This was clarified by accounting for the data on the effect of similar substitution on the coordination center reactivity in its dissociation upon interaction with proton [16]. The complexes could be arranged in the series (1) according to their stability in H_2SO_4 (that is, resistance to dissociation above 380 K).

$$CuPc(4\text{-}Cl)_4 < CuPc(4\text{-}NO_2)_4 < CuPc,$$
$$CuPc(4\text{-}Br)_4(5\text{-}NO_2)_4 < CuPc(3\text{-}Cl)_4 < CuPc(3\text{-}NO_2)_4. \quad (1)$$

In [16] it was established that the stability series (1) corresponded to the weakening of the σπ-type coordination bond. As not all the substituted complexes were more stable than CuPc, the induction σ-bond destabilizing effect was not the major factor affecting the complex stability. Since the 3-substituted complexes were again the most labile, and the octa-substitution gave the complex of intermediate stability, the other two factors, steric and conjugation, should have been accounted for. It is evident that the latter pair of effects acting oppositely in the cases of Cl and NO_2 substituents, stabilized the π-type bonds in the 4-substituted complexes, with the exception of the octa-substituted complex **V**, where the effects of different substituents compensated each other. The Cu^{2+} central ion, having the $3d^9$ electron configuration, was capable of both sharing the electron density with the vacant orbitals of the macrocycle, and intake the electron

Table 2. Proton addition energy E_{prot} and selected geometry parameters of the optimized isolated and protonated molecules of (phthalocyaninato)copper(II) and its chlorinated derivatives

Complex	$-E_{\mathrm{prot}}$, Kcal mol^{-1}	Bond length, Å					
		Cu–Ct	N^1–N^3 N^2–N^4	N^{m1}–N^{m3} N^{m2}–N^{m4}	N^{m1}–H^+ N^{m3}–H^+	N^{m2}–H^+ N^{m4}–H^+	P_N4 [a]
CuPc		0.0043	3.7990	6.8759			10.745
			3.7991	6.9177			
CuPcH$^+$(m)	211.72	0.0115	3.8007	6.8606			10.761
			3.8085	6.9266	0.9929		
CuPc2H$^+$(m), *trans*	149.84	0.0044	3.8044	6.8795	0.9969		10.760
			3.8044	6.8068	0.9933		
CuPc2H$^+$(m), *cis*	151.75	0.0097	3.8106	6.9189	0.9932	0.9941	10.775
			3.8085	6.8708			
CuPc3H$^+$(m)	83.74	0.0138	3.8046	6.8343	0.9956		10.766
			3.8079	6.8145	0.9957	0.9966	
CuPc4H$^+$(m)	28.12	0.0107	3.8095	6.8042	0.9962	0.9964	10.775
			3.8096	6.8346	0.9963	0.9988	
CuPc(3-Cl)$_4$		0.0115	3.7989	6.8731			10.746
			3.7991	6.9157			
CuPc(3-Cl)$_4$H$^+$(m)	215.70	0.0157	3.8042	6.8527	0.9961		10.762
			3.8052	6.9314			
CuPc(3-Cl)$_4$2H$^+$(m), *trans*	150.77	0.0169	3.8106	6.8649	0.9962		10.781
			3.8124	6.9241	0.9994		
CuPc(3-Cl)$_4$2H$^+$(m), *cis*	147.08	0.0157	3.8089	6.8711	0.9992	0.9996	10.777
			3.8115	6.9168			
CuPc(3-Cl)$_4$3H$^+$(m)	97.57	0.0157	3.8129	6.9019	1.0016	1.0012	10.792
			3.8169	6.9004	1.0004		
CuPc(3-Cl)$_4$4H$^+$(m)	31.49	0.0199	3.8063	6.7696	1.0001	1.0022	10.768
			3.8070	6.7949	1.0007	1.0030	
CuPc(4-Cl)$_4$		0.0086	3.7990	6.8754			10.739
			3.7990	6.9179			
CuPc(4-Cl)$_4$H$^+$(m)	211.32	0.0087	3.8087	6.8604	0.9930		10.806
			3.8007	6.9275			
CuPc(4-Cl)$_4$2H$^+$(m), *trans*	145.49	0.0092	3.8029	6.8048	0.9934		10.773
			3.8040	6.8666	0.9966		
CuPc(4-Cl)$_4$2H$^+$(m), *cis*	72.53	0.0385	3.7947	6.7391	1.1730	1.1735	10.736
			3.7945	6.7787			
CuPc(4-Cl)$_4$3H$^+$(m)	82.27	0.0097	3.8077	6.8808	0.9942	0.9950	10.751
			3.8102	6.8526	0.9944		
CuPc(4-Cl)$_4$4H$^+$(m)	38.54	0.0235	3.8233	6.9142	0.9956	0.9957	10.762
			3.8173	6.9142	0.9956	0.9957	

[a] Perimeter of the N^4 coordination plane.

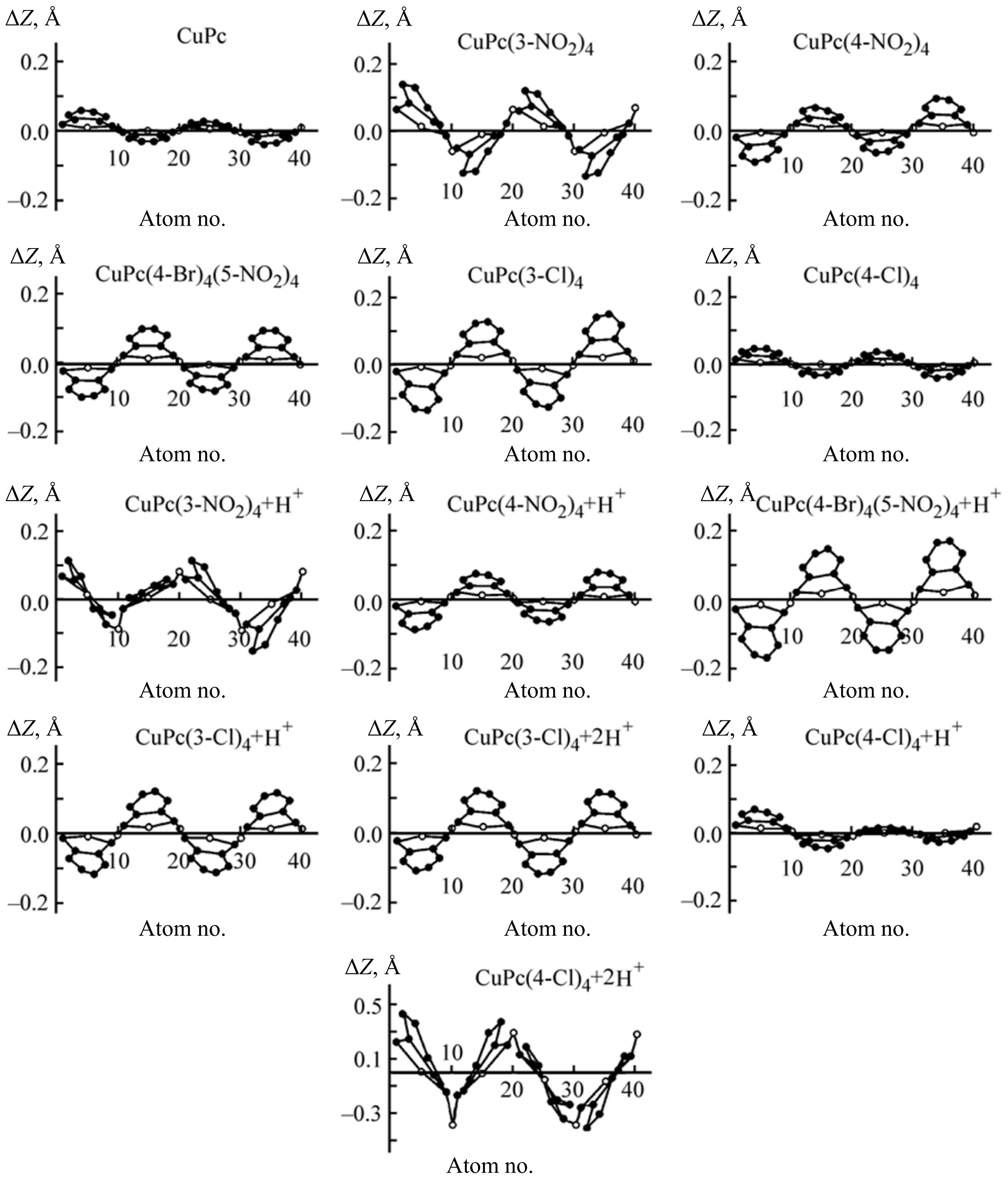
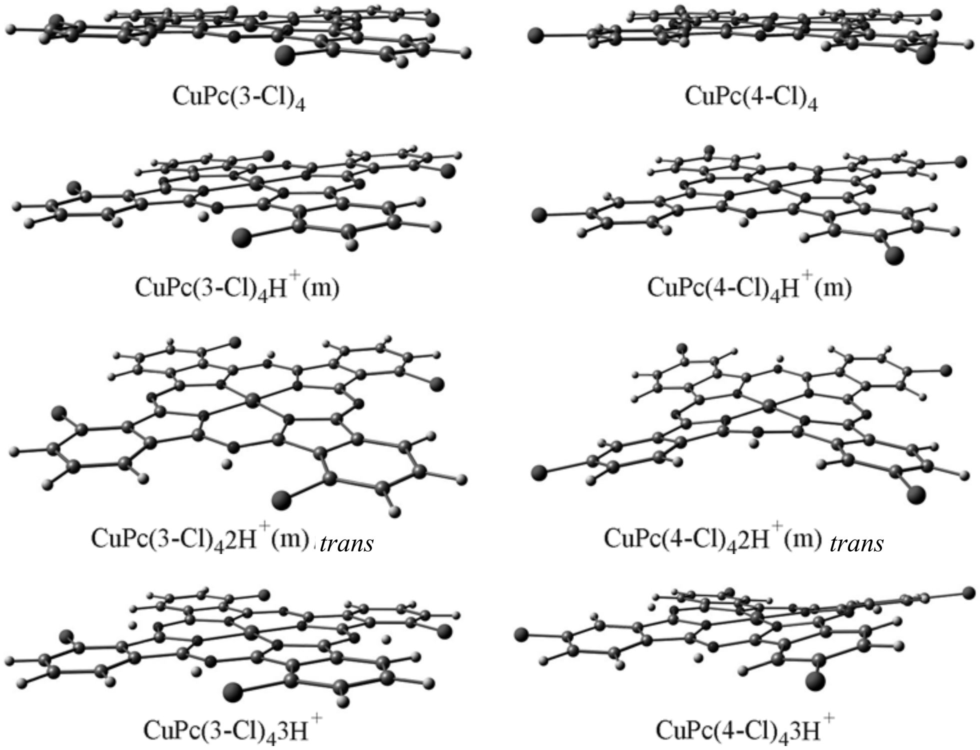


Fig. 2. Deviation of the skeletal atoms from the macrocycle mean plane along the Z axis, for (phthalocyaninato)copper(II), its substituted derivatives, and their mono- and diprotonated forms, according to PM3 simulation. (White circles) are nitrogen atoms, (dark circles) are carbon atoms.

from the occupied orbitals so that the *d*-shell was stabilized in $3d^{10}$ state.

As the exocyclic nitrogen atoms did not form such bonds with metal ion, the conjugation effects of Cl and NO_2 substituents affected them oppositely, which determined the relative basicity of the 4-substituted complexes **II**, **IV,** and **V**. Such manifestation of conjugation effects, confirmed in [22], was not of universal nature: The *C*-effects were not reflected in the values of the first protonation constants of CuPc substituted with phenyl and oxophenyl groups, or their thioanalogs [23].



$CuPc(3\text{-}Cl)_4$ $CuPc(4\text{-}Cl)_4$

$CuPc(3\text{-}Cl)_4H^+(m)$ $CuPc(4\text{-}Cl)_4H^+(m)$

$CuPc(3\text{-}Cl)_42H^+(m)$ *trans* $CuPc(4\text{-}Cl)_42H^+(m)$ *trans*

$CuPc(3\text{-}Cl)_43H^+$ $CuPc(4\text{-}Cl)_43H^+$

Fig. 3. Structures of (phthalocyaninato)copper(II) and its derivatives, as determined by PM3.

According to simulation results [13], the isolated CuPc molecule was characterized by low ring strain, symmetry of D_{4h}, and relatively flat structure with slightly noticeable saddle-type deformation. The Cu atom was deviated from the N_4 plane by 0.0043 Å. The N^1–N^3, N^2–N^4, N^{m1}–N^{m3}, N^{m2}–N^{m4} distances were pairwise equal (Table 2). The geometry of the four pyrrole cycles were not equivalent: 4 bond angles CNC were of 103.79°, 104.17°, 104.17°, and 103.79°. Skeletal atoms of the phthalocyanine macrocycle noticeably deviated from the mean plane of the macrocycle along the *Z* axis (Fig. 2). The total effective charge (q_{ef}) was positive (1.200 of electron unit charge) for the four coordinated nitrogen atoms and negative (–0.044) for the four exocyclic nitrogen atoms. Peripheral substitution of the CuPc molecule decreased its symmetry to that of D_{2h} and induced (or enhanced) the planar and torsion distortions of the macrocycle (Table 2, Figs. 2, 3), that were increasing in the series (2).

$$\begin{gathered}CuPc < CuPc(4\text{-}Cl)_4 < CuPc(4\text{-}NO_2)_4 \\ < CuPc(4\text{-}Br)_4(5\text{-}NO_2)_4 < CuPc(3\text{-}Cl)_4 < CuPc(3\text{-}NO_2)_4. \quad (2)\end{gathered}$$

3-substituted complexes were the most sterically strained. Saddle-type distortions were characteristic of the **I**, **II**, **IV**, and **V** molecules. The combination of saddle-type and ruffled distortions were observed in the case of **III** (Fig. 2). The planes of the functional groups location were oriented at an angle towards the plane of the fused benzene fragment (Fig. 3): in **III**, **IV**, and **V** the nitro group tilting angle was of 90°, 3°, and 26°, respectively. For all substituted complexes, the charge q_{ef} at the coordinated nitrogen atoms increased as compared with the unsubstituted CuPc, by 0.004–0.065 unit charge (u. ch.). The charge at the exocyclic nitrogen atoms changed differently upon substitution. In the cases of **IV** and **V** q_{ef} changed the sign and became equal to 0.021 and 0.032 of u. ch., respectively, whereas in the cases of **I**–**III** q_{ef} retained the sign and its absolute value decreased by 0.012–0.014 of u. ch. Taking into account the electron density distribution in the macrocycle, the series (3) was derived; in this series the value of q_{ef} at the exocyclic nitrogen atoms (reactive centers in the acidic protonation process) increased.

$$\begin{gathered}CuPc\ (–0.044\ u.ch.),\ CuPc(4\text{-}Cl)_4\ (–0.033\ u.ch.), \\ CuPc(3\text{-}Cl)_4\ (–0.029\ u.ch.),\ CuPc(3\text{-}NO_2)_4\ (–0.028\ u.ch.), \\ CuPc(4\text{-}NO_2)_4\ (0.021\ u.ch.), \\ CuPc(4\text{-}Br)_4(5\text{-}NO_2)_4\ (0.032\ u.\ ch.). \quad (3)\end{gathered}$$

In the cases of CuPc(4-Cl)$_4$ and CuPc(3-Cl)$_4$ the total charge q_{ef} at the exocyclic nitrogen atoms changed the sign to positive upon monoprotonation (0.555 and 0.578 u.ch., respectively) and further increased upon subsequent protonation stages.

The probability of existence of certain protonated forms could be estimated from their optimized geometry and energy parameters (Table 2, Fig. 2). Mono-protonation did not change the geometry of **I** and **II** significantly.

Addition of the second proton to CuPc(4-Cl)$_4$ significantly enhanced the steric strain of the macrocyclic ligand. Along with saddle-type deformation, ruffled and dome-shaped deformations were observed. Further protonation lead to quite distorted and unstable structures, thus pointing at a low probability of the third and forth protons addition in the case of 4-substituted complexes.

Stepwise protonation of CuPc(3-Cl)$_4$ did not lead to a significant change of type and degree of deformation (Figs. 2, 3). Thus, for complex **I** the forms protonated more than twice could exist. However, taking into account the protonation energy (E_{prot}) (Table 2), the addition of third and forth protons to this complex were unlikely as well. Indeed, the addition of the first and the second protons to exocyclic nitrogen atoms of **I** and **II** occurred with the energy comparable with the ammonia protonation (207 kcal mol^{-1}) [24, 25]. The likely formation of isomeric forms of the doubly protonated complex **I** was reflected in the complicated shape of the electron absorption spectrum Q-band (Fig. 1, Table 1).

EXPERIMENTAL

Template synthesis, purification, and identification of CuPc(3-Cl)$_4$, and CuPc(4-Cl)$_4$ complexes were described earlier [26]. Electron absorption spectra of the complexes solutions in sulfuric acid and in organic solvents were recorded at 298 K using Hitachi U-2000 and Agilent 8453 UV-Vis. H_2SO_4 concentration (chemically pure grade) was determined by acid-base titration (accuracy of ±0.12%).

Quantum-chemical simulation was performed by means of PM3 method [27–30] with complete geometry optimization. The pre-set gradient of 0.0004 kJ mol^{-1} A^{-1} was the break criterion. The starting approximation of the macrocycle geometry was a set of bond lengths and angles of the averaged metalloporphyrin structure [31].

ACKNOWLEDGMENTS

The work was financially supported by the Programs of fundamental research of the Presidium of the Russian Academy of Sciences No. 8 “Targeted synthesis of inorganic compounds with defined properties and functional materials based on them,” Russian Foundation for Basic Research (project no. 12-03-00967), and by Federal targeted program “Scientific and scientific-pedagogical staff of innovative Russia” for 2009–2012 (State contract no. 02.740.11.0106).

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