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Synthesis and Some Reactions of Silicon Phthalocyanine Anions

V. N. Myakov, V. A. Kuropatov, and T. I. Lopatina

Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
ul. Tropinina 49, Nizhnii Novgorod, 603600 Russia
e-mail: vmyakov@iomc.ras.ru

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Abstract—The reactions of $PcSi(OH)_2$ or $Me_3Si(OSiPc)_{1-3}OSiMe_3$ with Na or K afford anions of silicon mono-, di-, and triphthalocyanines (Pc_{1-3}) characterized by electronic absorption and EPR spectra. The reactions of the Pc_{1-3} anions with proton donors (H_2O and CH_3COOH), Me_3SiCl, and O_2 are carried out. The Pc_{1-3} anions in THF are reduced to the Pc_1^{3-} monophthalocyanine trianion with the partial rearrangement of the phthalocyanine into corrole. In benzene the reactions of Pc_{1-3} with Na or K occur only with an additive of crown ether (15C5): Na reduces Pc_1 to the Pc_1^{2-} dianion, Pc_2 and Pc_3 do not react with Na, and potassium reduces Pc_{1-3} to the Pc_1^{3-} trianion.

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INTRODUCTION

Metal phthalocyanines (MPc) are widely used in both fundamental and applied studies related to catalysis, molecular electronics, nonlinear optics, anticancer photodynamic therapy, and other areas [1, 2]. This variety of their use is due to the ability of the MPc macrocyclic ligand to undergo various redox transformations. For instance, they can be reduced consequently to the MPc^{4-} anion. In the case of main-group and many transition metals, additive anions are localized in the macrocycle rather than on the metal atom. The syntheses of the MPc anions, their electrochemistry, and electronic absorption and EPR spectra have been intensely studied during recent decades [3–5]. The ionic forms of phthalocyanines of 14 Group elements are studied to less extent. The studies on the electrochemical oxidation and reduction of silicon mono-, di-, tri-, and tetraphthalocyanines are known [6, 7]. However, no spectral data for the ions formed are found in these works.

We found that the silicon phthalocyanine mono- and dianions were formed in a strongly alkaline medium in the absence of reducing agents [8]. It would be of interest to compare the properties of these anions and the anions synthesized by the reaction of silicon phthalocyanines with Na or K with the properties of the well-studied anions of metal phthalocyanines.

EXPERIMENTAL

The compounds $PcSiCl_2$ and $PcSi(OH)_2$ (**I**) were synthesized according to a known procedure [9]. The compounds $HO(PcSiO)_2H$ (**II**) and $H(OSiPc)_3OH$ (**III**) were synthesized by the condensation of $PcSiCl_2$ and $PcSi(OH)_2$ (taken in a molar ratio of 1 : 1 when synthesizing compound **II** and 2 : 1 for the synthesis of compound **III**) in pyridine (Py) at 160°C for 2 h followed by the hydrolysis of the condensation product. Silicon trimethylsiloxyphthalocyanines (Pc_{1-3}) were synthesized by the reactions of compounds **I**–**III** with $(Me_3Si)_2NH$ in anhydrous Py

$$\textbf{I–III} + (Me_3Si)_2NH \longrightarrow Me_3Si(OSiPc)_{1-3}OSiMe_3. \quad (1)$$

The synthesis was carried out in sealed ampules at 170°C for 5 h. The crystals of $Me_3Si(OSiPc)OSiMe_3$ (Pc_1) and $Me_3Si(OSiPc)_2OSiMe_3$ (Pc_2) were washed with methanol to remove amorphous admixtures, and $Me_3Si(OSiPc)_3OSiMe_3$ (Pc_3) was isolated by chromatography on Al_2O_3 (using a $CHCl_3$–C_6H_6 (1 : 1) mixture as the eluent) followed by crystallization from a $CHCl_3$–C_6H_6 mixture. The purity of the Pc_{1-3} samples was monitored by the electronic absorption, IR, and EPR spectra.

Electronic absorption spectra (λ_{max}, nm): Pc_1, 355 (Soret band), 667, 606, and 640 (*Q* band); Pc_2, 330 (Soret band), 632 (*Q* band); Pc_3, 328 (Soret band), 618 (*Q* band). IR, cm^{-1}: 1250 (SiMe), 1030 ($Me_3SiOSiPc$), 980–1000 (PcSiOSiPc). ^1H NMR ($CDCl_3$) δ, ppm: Pc_1, 9.65 m (3,6-H), 8.35 m (4,5-H), –2.81 s (H–$SiMe_3$); Pc_2, 9.03 m (3,6-H), 8.35 m (4,5-H), –3.88 s (H–$SiMe_3$); Pc_3, 8.53 m (3,6-H) outer, 8.07 m (4,5-H) outer, 8.41 m (3,6-H) inner, 8.36 m (4,5-H) inner, –4.35 s (H–$SiMe_3$).

The reduction of $Me_3Si(OSiPc)_{1-3}OSiMe_3$ was carried out in sealed evacuated ampules soldered to an optical cell and an EPR tube. For each entry, 1–3 mg of Pc_{1-3}, 8–10 mg of crown ether (15C5), 10–15 mg of Na (K), and 6 ml of THF or benzene were taken. Benzene and THF were distilled and kept over sodium ketylbenzophenone, and they were dosed into the ampules by vacuum condensation. The experiments were carried out at room temperature with magnetic stirring of the reaction mixture. As the color of the solution changed, a portion of the

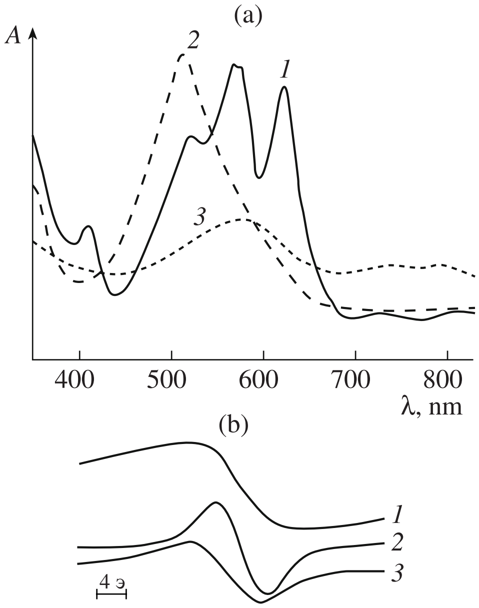

Fig. 1. Changes in the (a) electronic absorption spectra and (b) EPR signal of the solution obtained by the reaction of $PcSi(OSiMe_3)_2$ with Na in THF at 20°C after (*1*) 1.5, (*2*) 3.0, and (*3*) 7 h.

reaction mixture was poured to the cell. Then the solvent from the reaction ampule was condensed into the cell until the necessary absorbance of the solution was achieved. The absorbance was monitored, recording the electronic absorption spectra. The solution was poured to the tube, and the EPR spectrum was recorded. The reactions of the Pc_{1-3} anion with H_2O, CH_3COOH, Me_3SiCl, and O_2 were carried out at room temperature. Water, CH_3COOH and Me_3SiCl were dosed to the ampule in vacuo, the reaction mixture was stirred for 5–10 min, and the electronic absorption spectra were recorded.

Electronic absorption spectra were recorded on a Specord M40 spectrophotometer or on a Perkin Elmer Lambda 25 spectrometer. ^1H NMR spectra were measured on a Bruker DPX 200 spectrometer. IR spectra were recorded on a Specord 75IR spectrophotometer. EPR spectra were obtained on a Bruker EMX-8/2.7 instrument.

RESULTS AND DISCUSSION

Reactions of Pc_{1-3} in THF. The changes in the electronic absorption spectra of the solution obtained during the reaction of Pc_1 with sodium in THF are shown in Fig. 1. In the spectrum of this solution, the *Q* band of the starting phthalocyanine disappears and two intense absorption bands with λ_{max} = 580 and 620 nm and low-intensity absorptions at 409, 725, and 860 nm appear. The doublet at 580 and 620 nm disappears with time, and a broad band with λ_{max} = 515 nm appears. The blue color of the reaction mixture changes consecutively to dark blue, violet, and red. The subsequent changes are due to the shift of this absorption band to the long-wave spectral region. In the electronic absorption spectrum of the final product, an absorption band at 590 nm and two low-intensity bands at 743 and 795 nm appear. The color of the reaction mixture changes from red to violet and then to dark blue.

When the Pc_2 diphthalocyanine and Pc_3 triphthalocyanine are reduced, the color of the reaction mixture changes in the same order as for Pc_1 reduction: blue, dark blue, violet, and red and then again violet and dark blue. The absorption band of Pc_2 shifts from 632 nm consecutively to 578, 550, and 515 nm and then back to the long-wave spectral region, λ_{max} of the absorption bands of the final products being 590, 743, and 795 nm. The electronic absorption spectra of the solutions obtained by Pc_3 reduction are distinguished by the absorption band of the starting Pc_3 (618 nm), whereas the absorption bands of the intermediate anions and the final anion (λ_{max} = 590, 743, and 795 nm) remain unchanged.

The electronic absorption spectra of the metal phthalocyanine anions $(MPc)^{n-}$ (n = 1–4; M = Mg, Zn, Ni, et al.) were thoroughly analyzed, and their high specificity and similarity make it possible to reliably interpret the data on these anions [10]. The spectra of the anions obtained by us using the reduction of the Pc_1 monophthalocyanine agree well with the data for the MPc^{n-} anions [10]. The doublet at 580 and 620 nm corresponds to the Pc^- monoanion, the absorption band with λ_{max} = 515 nm corresponds to the Pc^{2-} dianion, and the band with 590 nm with two satellites (743 and 795 nm) corresponds to the Pc^{3-} trianion. The reduction of Pc_{1-3} is a consecutive process

$$Pc_{1-3} + e \longrightarrow Pc^{-}_{1-3} + e \longrightarrow Pc^{2-}_{1-3} + e \longrightarrow Pc^{3-}_{1-3}. \quad (2)$$

For this reason, the first new band with $\lambda_{max} \approx 580$ nm for the reduction of the Pc_2 diphthalocyanine can be attributed to the Pc^{-}_{2} monoanion as the first reduction product. The second new band with λ_{max} = 550 nm is assigned to the Pc^{2-}_{2} dianion, and the first new absorption band with λ_{max} = 580–590 nm for the reduction of the Pc_3 triphthalocyanine is associated with the Pc^{-}_{3} monoanion. The absorption band of the Pc^{2-}_{3} dianion lies, most likely, in a range of 575–590 nm, and we failed to distinguish the absorption bands of Pc^{-}_{3} and Pc^{2-}_{3}.

The band with λ_{max} = 515 nm, indicating the formation of the Pc^{2-}_{1} monophthalocyanine dianion, appears in the electronic absorption spectrum of the solution upon the formation of the Pc_2 and Pc_3 anions. Therefore, the reduction is accompanied by the fragmentation of the dimer and trimer to form the monophthalocyanine anions, and the Pc^{3-}_{1} monophthalocyanine trianion is the final product of Pc_2 and Pc_3 reduction. It is known [11] that silicon oligophthalocyanines $(OSiPc)_m$ are stable during oxidation but degrade to monophthalocyanines upon electrochemical reduction.

The EPR spectra of the Pc_1^{n-} anions represent single lines with *g* close to the *g* factor of a free electron (Fig. 1b). The width and shape of the signals depend on the degree of Pc_1 reduction. It was unexpected that the reduction of the Pc_1^- paramagnetic monoanion to the Pc_1^{2-} dianion did not result in the disappearance of the EPR signal; i.e., the dianion is most likely paramagnetic. It was experimentally found [4] that the MPc^{2-} metal dianions (M = Mg, Zn, Ni) were diamagnetic, although the triplet ground state was theoretically predicted for them [10]. The EPR signal of the Pc^{3-} trianion disappears several days after, and the electronic absorption spectrum of the trianion remains unchanged. In the reactions of Pc_2 and Pc_3 with Na, the EPR signal appears with the formation of the Pc_2^- and Pc_3^- monoanions. The signal does not disappear upon the formation of the dianions, and the signal of the Pc^{3-} trianion (the final reduction product) disappears gradually, as in the reaction of Pc_1.

The reactions of Pc_{1-3} with potassium in THF occur with nearly the same rate as that with sodium, and the changes in the electronic absorption and EPR spectra are similar.

Reactions of Pc_{1-3} in benzene. Without an additive of 15C5, Pc_{1-3} react with neither Na, nor K in benzene. It is most likely that the role of the crown ether is a decrease in the activation energy of the electron transfer due to the specific solvation of the Na^+ cation as the counterion of the Pc_1^- and Pc_1^{2-} anions. Sodium reduces Pc_1 in the presence of 15C5 only to the red Pc_1^{2-} dianion (λ_{max} = 525 nm), and Pc_2 and Pc_3 do not react with Na. Silicon monophthalocyanine is more electron-withdrawing than silicon di- and triphthalocyanines. The reduction of Pc_1 to Pc_1^{2-} in benzene at 20°C takes 4–5 days, whereas this reaction in THF proceeds within several hours.

For the reaction of $PcSi(OH)_2$ with Na, the rate of Pc^- reduction to Pc^{2-} is higher than the rate of $PcSi(OH)_2$ dissolution. There is no EPR signal of the reaction mixture, because the concentration of the dark blue Pc^- monoanion (λ_{max} = 580 and 620 nm) is low and no EPR signal is observed for the Pc^{2-} dianion in benzene. When $PcSi(OSiMe_3)_2$ that is moderately dissolved in benzene is reduced, the Pc_1^{2-} dianion appears in the reaction mixture only after Pc_1 is consumed, because the latter rapidly oxidizes the Pc_1^{2-} dianion to the Pc_1^- monoanion

$$Pc_1 + Pc_1^{2-} \longrightarrow 2Pc_1^-. \qquad (3)$$

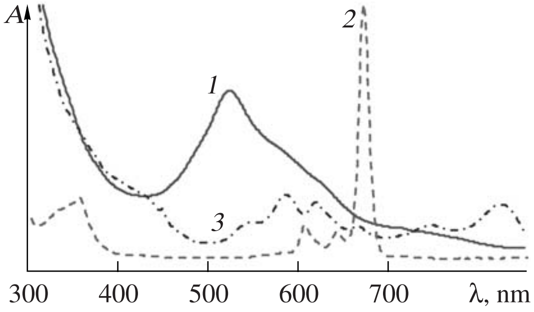

Fig. 2. Electronic absorption spectra of the Pc_1^{2-} dianions (*1*) before and (*2*, *3*) after their interaction with O_2: (*2*) Pc_1^{2-} were synthesized in THF by the reactions of $PcSi(OSiMe_3)_2$ (Pc_1) and $PcSi(OH)_2$ with Na (K) and in benzene by the reaction of Pc_1 with Na and (*3*) Pc_1^{2-} were synthesized in benzene by the reaction of $PcSi(OH)_2$ with Na (K) or by the reaction of Pc_1 with K.

The EPR signal appears upon the formation of the Pc_1^- monoanion and disappears after the reduction of the monoanion to the dianion.

The reactions of $PcSi(OH)_2$ and $PcSi(OSiMe_3)_2$ (Pc_1) with potassium proceed almost similarly, because Pc_1 with a KOH admixture is hydrolyzed to $PcSi(OH)_2$. The Pc^{2-} dianion rapidly appears in the reaction mixture and is gradually transformed into the blue Pc^{3-} trianion (λ_{max} = 606, 760, and 804 nm). The EPR signal (a singlet without HFS) appears and grows with an increase in the concentration of the Pc^{3-} trianion. A blue paramagnetic precipitate is formed in the ampule, the solution is gradually decolorized, and the EPR signal of the solution disappears.

Reactions of the Pc_{1-3} anions with proton donors, Me_3SiCl, and O_2. The Pc_1^{n-} monophthalocyanine anions obtained with Na or K in both THF and benzene regenerate Pc_1 upon the interaction with the proton donors (H_2O, CH_3COOH) or with Me_3SiCl.

The MPc^{2-} metal phthalocyanine dianions regenerate the starting MPc upon the interaction with O_2, donating to oxygen electrons received from the metal atom [4]. The Pc_1^{2-} dianions synthesized by the reduction of Pc_1 with Na (K) in THF or with Na in benzene under the action of O_2 also regenerate Pc_1 (Fig. 2, curve *2*). However, it turned out that the Pc_1^{2-} dianions formed by the reduction in benzene of $Pc\text{-}Si(OH)_2$ with sodium (potassium) or by the reduction of Pc_1 with potassium react with O_2 in a different manner (Fig. 2, curve *3*). We earlier found [8] that the Pc_1^{2-} dianions, which were formed by

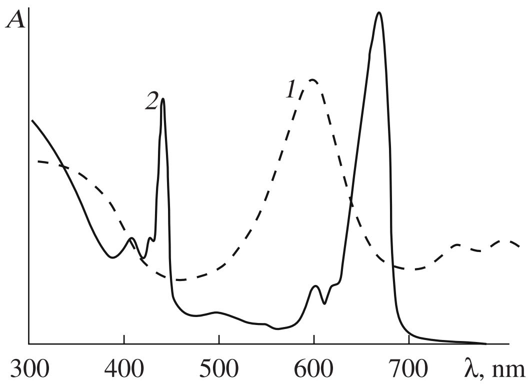

Fig. 3. Electronic absorption spectra of the Pc^{3-} trianion in THF (*1*) before and (*2*) after its reaction with O_2 or Me_3SiCl.

the reaction of $PcSi(OH)_2$ with KOH in the presence of the crown ether, reacted with O_2 in such a way

$$\mathrm{PcSi(OH)_2 + 2KOH \xrightarrow{15C5}} \\ \longrightarrow [\mathrm{PcSiO_2^{2-}}](\mathrm{K^+ \cdot 15K5})_2 + 2\mathrm{H_2O}\uparrow, \qquad (4)$$

$$[\mathrm{PcSiO_2^{2-}}]\,(\mathrm{K^+ \cdot 15K5})_2 \rightleftharpoons [\mathrm{O(Pc^{2-})SiO}]\,(\mathrm{K^+ \cdot 15K5})_2. \qquad (5)$$

Dianion **I** is formed due to the intramolecular transfer of the electron density to the macrocycle from the oxygen atoms of the $(Pc)SiO^-K^+$ siloxanolate in which the degree of charge separation increases due to the solvation of the K^+ cation by the crown ether. The same reactions with KOH and 15C5 are characteristic of Pc_2 and Pc_3, which form the corresponding dianions according to Eqs. (4) and (5) after hydrolysis to $H(OSiPc)_2OH$ or $H(OSiPc)_3OH$ [12, 13].

Evidently, the $PcSi(OK)_2$ and $PcSi(ONa)_2$ siloxanolates are also formed by the reaction of $PcSi(OH)_2$ with Na (K) and by the reduction with potassium of Pc_1, which is hydrolyzed to $PcSi(OH)_2$ with a KOH admixture

$$\mathrm{PcSi(OH)_2 + 2M \longrightarrow PcSi(OM)_2 + H_2\ (M = Na, K).} \qquad (6)$$

In the presence of the crown ether, the $PcSi(OM)_2$ siloxanolates are transformed into the dianions via reaction (5), and an electron is transferred to the macrocycle through the O–Si–Pc bonds. The intramolecular reduction of Pc_1 with Na in benzene is impossible because of the blocking effect of the $OSiMe_3$ group. Probably, the electron is transferred via the outer-sphere mechanism and, hence, the reaction of the dianion with O_2 regenerates the starting phthalocyanine as in the reactions of MPc^{2-} (Fig. 2, curve *2*).

After O_2 or Me_3SiCl contacted with the Pc^{3-} trianions, which were synthesized by the reduction of Pc_{1-3} in THF, the products of the corrole structure were observed in the reaction mixture in addition to the Pc_1 monophthalocyanine (Fig. 3, curve *2*; Soret band with λ_{max} = 442, 430, and 412 nm). No corroles are formed upon the reduction of Pc_{1-3} in benzene: they are absent from the products of the reaction with O_2 of the $SiPc^{2-}$ dianions formed both in THF and benzene. The reduction of the phthalocyanine to the $SiPc^{3-}$ trianion destabilizes the phthalocyanine, and the loss of the axial ligand at the silicon atom and *meso*-nitrogen atom becomes possible to form tetrabenzotriazacorrole [14, 15]. This transformation occurs in THF and does not occur in low-polarity benzene.

Thus, the reduction of silicon phthalocyanine by Na or K in both THF and benzene affords the anions, whose electronic absorption spectra are in good agreement with the published spectra of the phthalocyanine anions of Mg, Zn, Ni, and other metals. The transfer of electrons to the macrocycle from the axial $(Pc)SiO_2^{2-}$ siloxanolate anion affords the Pc^{2-} dianions, which probably degrade upon the interaction with O_2 [8]. The outer-sphere reduction produces the Pc^{2-} dianions, which regenerate the phthalocyanine in the reaction with O_2. Thus, in spite of the similarity of the electronic absorption spectra of the Pc^{2-} dianions, their properties are different. The rearrangements of the phthalocyanine structure into the corrole structure occur with a noticeable rate in the Pc^{3-} trianions.

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