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Preparation and Some Properties of Ionic Salts of C_{60}^{-} and C_{60}^{2-} Fullerides with Phthalocyanine Cations

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Abstract—Ionic fullerides of C_{60}^{-} and C_{60}^{2-} with the silicon phthalocyanines cations were obtained in the reaction of $PcSi(OH)_2$ with fullerene C_{60} in the presence of KOH in DMSO or in xylene and THF with the addition of 15C5 crown ether. The fullerides were characterized by electron absorption, ^1H NMR and electron spin resonance spectra, and their reaction with O_2 and CF_3COOH were carried out.

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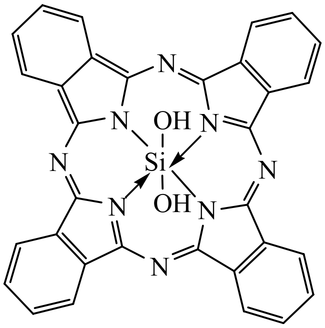
A wide variety of physical, chemical, and catalytic properties of phthalocyanines due to their unique electronic system created by 18-*p*-electron aromatic macrocycle with four tetrapyrrole fragments conjugated with four benzo groups joined by four nitrogen atoms, and coordinated to the metal atom [1, 2].



$PcSi(OH)_2$

Metallophthalocyanines MPc are capable of a variety of redox transformations. They can be reduced in succession to four-charged anion MPc^{4-} or oxidized to the mono- or dication, therewith, in the phthalocyanines of nontransition and of many transition metals the additional electrons are localized in the macrocycle. The absorption spectra of metal phthalocyanine anions are very characteristic for each anion and are highly repeatable for different metals, so the electronic spectroscopy is regarded as the primary method of identification of the anions $(MPc)^{n-}$ [3–5].

Silicon phthalocyanines (SiPc) are converted into mono- and dianions without a reducing agent while reacting with KOH in *o*-xylene in the presence of 15C5 crown ether, as a result of intramolecular transfer of electron density on the macrocycle from the siloxanate oxygen atom $(Pc)SiO^{-}K^{+}$. The degree of charge separation increases due to the solvation of the cation K^{+} with the crown ether. The free silicon *d*-orbitals provide *n*–σ–π interaction of the electron pair of axial oxygen atoms and π-electron system of the phthalocyanine macrocycle [6]. The dianions thus obtained form red D–A complexes $[(Pc^{2-})\cdot PcSiX_2]$ or $[(Pc^{2-})\cdot O_2]$, in which the silicon phthalocyanine dianion Pc^{2-} is a donor and the initial SiPc or oxygen is an acceptor of electron density [7].

It seemed interesting to study the interaction of Pc^{2-} dianions with the electron acceptor like fullerene C_{60}. There is a large number of publications on the synthesis and properties of compounds containing anions C_{60}^{n-} (n = 1–12), some of which are organic metals, superconductors, or ferromagnetics [8, 9]. The C_{60} is widely used in functional molecular ensembles, e.g., combined with metal phthalocyanines for the construction of photovoltaic cells [10–12].

The metal phthalocyanines in the ground state form with the fullerene C_{60} only contact complexes, so the EAS of a reaction mixture $PcSi(OSiMe_3)_2$ or $PcSi(OH)_2$ with the C_{60} is an additive superposition of the spectra of the mixture components containing no new absorption bands [13].

At pouring together of xylene solutions of the dianion of phthalocyanine Pc^{2-} and C_{60} in the EAS of the reaction mixture the absorption band of Pc^{2-} disappears and appears a series of absorption bands in the near infrared at wavelengths of 1075, 1035, 994, 940, and 916 nm that belong to the C_{60}^{-} fullerene monoanion [14–17]. It is obvious that the reduction of C_{60} to C_{60}^{-} is due to the electron transfer from Pc^{2-} dianion. In the presence of KOH and the crown ether the C_{60}^{-} monoanion is formed also in a reaction of C_{60} with $PcSi(OH)_2$ in the absence of air in xylene or THF. In this case, the reducing agent for C_{60} are the dianions (Pc^{2-}), monoanion (Pc^{-}), or D–A complexes SiPc, which are formed in the reaction of $PcSi(OH)_2$ with KOH and the crown ether. The interaction of PcSi $(OH)_2$ with C_{60} in DMSO in the presence of KOH results in the appearance in the EAS of the reaction mixture of an absorption band with a wavelength of 950 nm, which belongs to the fullerene dianion C_{60}^{2-} [14–17]. Thus, the reaction of silicon phthalocyanine dianion $SiPc^{2-}$ with C_{60} fullerene in xylene, like the reaction of $PcSi(OH)_2$ with C_{60} in the presence of KOH and crown ether in either xylene, or THF, or DMSO leads to the formation of ionic fullerides C_{60}^{-} or C_{60}^{2} with the Pc^{2-} dianions as the cations.

Reaction in xylene. The reaction course depends on the relative concentration of $C_{60}/PcSi(OH)_2$, the presence or absence of solid alkali in the reaction mixture, and is complicated by precipitation of the formed C_{60}^{-}, therewith, the precipitate and solution com-positions become different to the end of the experiment.

In the reaction of equimolar amounts of Pc^{2-} and C_{60} in solution in the absence of KOH pellets the dianion Pc^{2-} (λ_{max} 528 nm) is transformed into the monoanion Pc^{-} (λ_{max} 580, 620 and 943 nm), which then reduces C_{60} to C_{60}^{-}. In the spectrum of the precipitate after its dissolution in THF in addition to the absorption bands of C_{60}^{-} there is a strong absorption due to the monoanion Pc^{-} (Fig. 1). In the presence of KOH pellets the concentration of monoanion Pc^{-} in the solution increases rather than decreases, and then the concentration of the Pc^{2-} dianion increases. After replacing xylene by THF and dissolution of the precipitate, in the spectrum of the reaction mixture a strong peak appears of the fullerene dianion C_{60}^{2-} and the absorption band corresponding to Pc^{2-} greatly increases. The appearance of the Pc^{-} monoanion and then the Pc^{2-} dianion of silicon phthalocyanine indicates that in the course of the reactions there is a deficit of C_{60}, probably due to the consumption of the fullerene in a side reaction.

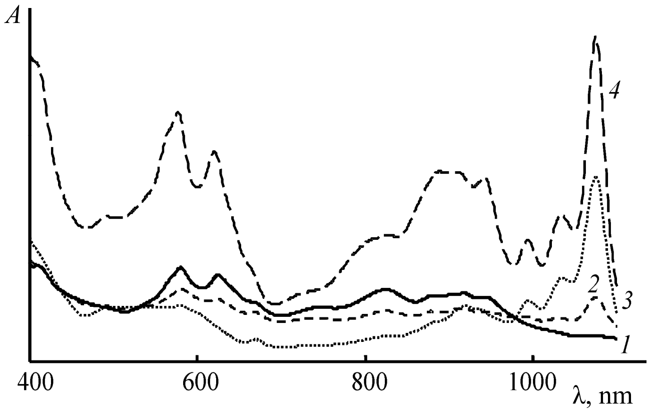


Fig. 1. EAS of the solution of reaction mixture in xylene in the reaction of C_{60} with $PcSi(OH)_2$ (1:1) in the presence of KOH and 15C5 after 60 min (*1*), 240 min (*2*), 24 h (*3*) and in 15 min after the replacement of xylene by THF (*4*). The reaction was carried out in an evacuated ampule sealed to the cell.

In the experiments with excess C_{60} ($C_{60}/SiPc \geq 2:1$) in the presence of KOH pellets after replacing xylene by THF for a few minutes the C_{60}^{-} dianion is reduced to C_{60}^{2-} . In a similar experiment in the absence of KOH pellets the transformation of the monoanion C_{60}^{-} into C_{60}^{2-} dianion after replacing xylene does not occur.

In the absence of air the C_{60}^{-} preparation can be carried out by the reaction of C_{60} and $PcSi(OH)_2$ directly, bypassing the stage of obtaining Pc^{2-}. The reaction scheme is the same, the reducing agents for C_{60} are silicon phthalocyanine mono- and dianions Pc^{-} and Pc^{2-}, formed in the reaction of $PcSi(OH)_2$ with KOH and crown ether. In this case, the presence of KOH pellets in the reaction is necessary to adsorb H_2O.

Thus, the first product in the reaction of silicon phthalocyanine dianion Pc^{2-} with C_{60} in xylene is the monoanion of the fullerene C_{60}^{-}. The presence of KOH pellets in the reaction accelerates both formation of C_{60}^{-} and the reduction of C_{60}^{-} to C_{60}^{2-} after replacing xylene by THF.

Reaction in THF. The reaction of C_{60} with PcSi $(OH)_2$ was performed in the presence of crown ether 15C5, both with or without KOH. In the latter case, the KOH was added to the reaction mixture as an THF extract of the KOH complex with the crown ether. We varied the relative concentrations of C_{60} $[C_{60}/PcSi(OH)_2]$ and the crown ether $[15C5/PcSi(OH)_2]$.

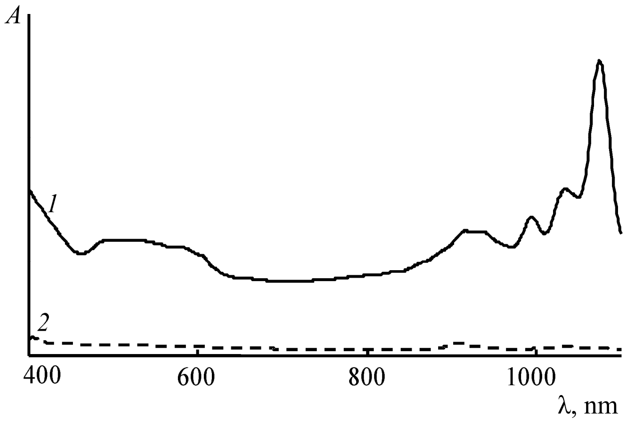


Fig. 2. EAS of the reaction mixture in the reaction of C_{60} with $PcSi(OH)_2$ (3:1) in the presence of 15C5 in THF in the absence of KOH after 24 hours and 6 months (*1*) and after reaction with CF_3COOH (*2*).

In the reactions with the C_{60}/SiPc at the ratio from 1:1 to 5:1 and the crown ether/$PcSi(OH)_2$ concentration ratio from 3:1 to 40:1 initially C_{60}^- fulleride is formed, which in THF has a crimson color (Fig. 2). In reactions with 20–40-fold excess of the crown ether, i.e., with a large excess of KOH, the absorption of C_{60}^- decreases with time, and in the spectrum the absorption bands appear of the Pc^- monoanion and a D–A complex of the silicon phthalocyanine, and further, the bands of the dianions Pc^{2-} and C_{60}^{2-}. An increase in the relative concentration C_{60}/SiPc to (3–4):1 stabilizes C_{60}^- anion, C_{60} blocks the reaction (2) of the Pc^{2-} dianion with the parent $PcSi(OH)_2$ that competes with the reaction (1) of the C_{60}^- formation.

$$Pc^{2-} + C_{60} \rightarrow C_{60}^-, \tag{1}$$

$$Pc^{2-} + PcSi(OH)_2 \rightarrow \text{D–A complex } \mathbf{I}. \tag{2}$$

To obtain the C_{60}^- fulleride it is optimal to perform the reaction of $PcSi(OH)_2$ with a threefold to fourfold excess of C_{60} and the crown ether/$PcSi(OH)_2$ ratio (5–10):1 in the absence of KOH. The C_{60}^- fulleride resulting in such conditions does not change at keeping in a sealed ampule for several months (Fig. 2). In reactions at the equimolar C_{60}/$PcSi(OH)_2$ ratio the C_{60}^- monoanion concentration gradually falls, and C_{60}^{2-} anions and D–A complexes of SiPc appear.

Reaction in DMSO. At stirring $PcSi(OH)_2$ with C_{60} in DMSO in the presence of KOH in the absence of air the color of the reaction mixture during 60–120 min varies from blue, dark blue, to brownish–green and brown. The absorption spectrum of the resulting reaction mixture (Fig. 3, curve *2*) is identical to that of the C_{60}^{2-} fulleride shown in [14–16]. In the absence of KOH, the reaction does not occur, so it is obvious that the reducing agent in the reaction is the D–A complex of silicon phthalocyanine, which is known to be formed in DMSO in the reaction of $PcSi(OH)_2$ with KOH [7]. As expected, a preliminary synthesized D–A complex reacts with C_{60}^- to form C_{60}^{2-} (Fig. 3), while in the reactions of C_{60} with $PcSi(OH)_2$ first the D–A complex I (λ_{max} 540,580,740 and 825 nm) is formed which reduces C_{60} to C_{60}^{2-} fulleride.

In reactions with equimolar amounts of C_{60} and $PcSi(OH)_2$ the D–A complex concentration grows faster than the C_{60}^{2-} consumption. Like the reaction in THF, the C_{60} is consumed in a side reaction, and at the end of the experiment the reaction mixture contains Pc^{2-} dianion and D–A complex II (λ_{max} ~815 and 890 nm), and fulleride C_{60}^{2-} is absent. A more complete conversion to the fulleride C_{60}^{2-} can be achieved when in the reaction with $PcSi(OH)_2$ two- or four-fold excess of C_{60} is taken. The C_{60} excess accelerates the reaction of the C_{60}^{2-} formation (3) and blocks the competing reaction (4):

$$\mathbf{I} + C_{60} \rightarrow C_{60}^{2-}, \tag{3}$$

$$\mathbf{I} + \text{KOH/DMSO} \rightarrow \mathbf{II}. \tag{4}$$

Complex D–A (**II**) is less active in the reduction of C_{60} than D–A (**I**). Therefore, the admixture of complex D–A (**II**) seems to be always present in fulleride C_{60}^{2-}.

Optimal for obtaining C_{60}^{2-}, is the reaction at a ratio of C_{60}/$PcSi(OH)_2$ (2–4):1 in the presence of KOH pellets, which absorb H_2O formed in the reaction. This is necessary because fulleride C_{60}^{2-} is a strong base and reacts immediately with H^+ donors [8, 17]. In DMSO, C_{60} is reduced to the dianion C_{60}^{2-}, while the C_{60}^- monoanion is formed in small quantities, even in reactions with a four-fold excess of C_{60}. The C_{60} fullerene does not oxidize the C_{60}^{2-} dianion to the C_{60}^- monoanion. Obviously, the C_{60}^{2-} dianion is stabilized in DMSO to a greater extent than the monoanion.

Thus, obtaining the C_{60}^- and C_{60}^{2-} fullerides in xylene is problematic, but it may be interesting to elucidate the details of the reaction of the fullerene C_{60} reduction. Preparation of C_{60}^- fulleride is quite convenient to carry out in THF, and C_{60}^{2-}, in DMSO. We failed to find the conditions for obtaining C_{60}^{2-} in THF, as in the reactions besides C_{60}^{2-} anions, or a D–A complex with SiPc are formed. In the presence of KOH pellets in reactions of $PcSi(OH)_2$ and C_{60} in equimolar amounts regeneration of the original SiPc dianion proceeds in all the solvents: xylene, THF, and DMSO.

The Pc^{2-} dianions obtained by the reduction of SiPc with an alkali metal readily release extra electrons, regenerating the phthalocyanine original structure [18]. The situation is different when in the reaction with C_{60} the Pc^{2-} dianion is involved, in which two additional electrons in the macrocycle appear due to an intramolecular reorganization of the electronic structure of phthalocyanine. The transfer of electrons from the Pc^{2-} dianion to the C_{60} fullerene not only regenerates the structure of the phthalocyanine, but also leads to products which, apparently, are not known in the literature.

It was shown [19] that the ease of oxidation of an electron donor depends in many respects on the ability of delocalization of a positive charge arising at the electron transfer to the acceptor. Apparently, the multi-electronic structure of silicon phthalocyanine provides such a delocalization. It is also important that the forming cation and anion were quite stable and did not react with each other to form, for example, the radical $K–C_{60}^{\bullet}$. The formation of a covalent bond between the phthalocyanine and C_{60} is difficult because of the repulsion of the phthalocyanine benzoid fragments and the fullerene core.

A feature of the reactions of C_{60} is a low reorganization energy of the nuclei and of the solvent, because the structure of the rigid C_{60} core changes little both in ground and reduced states, and achieving the consistence of the reduced states with the solvent molecules does not require large expenditures [20]. The same can be attributed to the reactions of metal phthalocyanines, whose 18-π-electron aromatic system forms a rigid structure, whose geometry is almost unchanged at the one-electron oxidation or reduction [5]. The energy expenditure required for the separation of positive and negative charges in the fullerides C_{60}^{-} and C_{60}^{2-} obviously is fully compensated by the energy of solvation of the formed $[(SiPc)^{+}\cdot(C_{60})^{-}]$ dipoles by polar THF and DMSO.

The transformation of $PcSi(OH)_2$ into the Pc^{2-} dianion leads to the disappearance of the intense absorption bands in the region of 600–670 nm (a *Q*-band) and the appearance of absorption bands with λ_{max} 515–525 nm. The D–A I complex of the silicon phthalocyanine gives rise in the visible region of the spectrum the charge-transfer bands with λ_{max} 540, 580, 740 and 825 nm. The metal phthalocyanine cation radicals, like $ClZn^{II}(Pc^{+})$, also have strong absorption bands in the region of 700–400 nm [21]. The cation, that is, the phthalocyanine part of the complexes of C_{60}^{2-} and C_{60}^{-} does absorb in the visible region, as evidenced by the complete identity of the absorption spectra of C_{60}^{-} and C_{60}^{2-} obtained in this work, and by the electrochemical study of solution in CH_2Cl_2 in the presence of $n\text{-}Bu_4NClO_4$ as the supporting electrolyte [14, 17]. This is direct evidence of a profound restructuring of the electronic structure of silicon phthalocyanine at the formation of the fullerides C_{60}^{-} and C_{60}^{2-}.

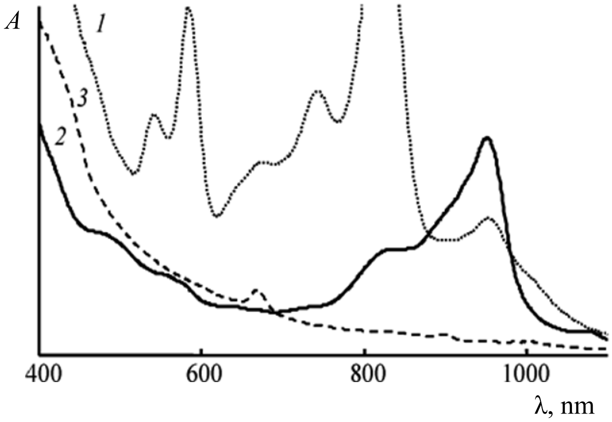


Fig. 3. EAS of the reaction mixture in the reaction of C_{60} with $PcSi(OH)_2$ (4:1) in the presence of KOH in DMSO: (*1*) after 15 min, (*2*) in 20 h after introduction of C_{60} in the cell and dilution of the reaction mixture twice, (*3*) in 15 min after reaction with O_2 or CF_3COOH.

On the other hand, the lack of absorption in the visible region of the spectrum shows that the SiPc in the fullerides of C_{60}^{-} and C_{60}^{2-}, apparently, is a donor of two electrons. At the one-electron transfer of the phthalocyanine part of the fullerides a radical cation would form with absorption in the visible spectrum and with the ESR spectrum different from that of C_{60}^{-} and C_{60}^{2-} fullerides. The ESR signals of the C_{60}^{-} and C_{60}^{2-} fullerides obtained in this paper are entirely consistent with the literature [8, 17]. The values of $g = 1.99997$–2.00000 are significantly less than the $g = 2.00230$ for most organic radicals, and the width of the signals is within 0.6–1.3 Oe. At the two-electron transfer the silicon phthalocyanine dianion of the C_{60}^{-} fulleride is coordinated with two molecules of C_{60} and in C_{60}^{2-} fulleride, with one molecule of C_{60}. We were unable to isolate crystalline samples of fullerides, therefore the structure of fullerides is only tentative.

Reaction of C_{60}^{-} with CF_3COOH and O_2. Oxygen is not very active in the reaction with C_{60}^{-} fulleride, the fulleride absorption bands remain almost unchanged

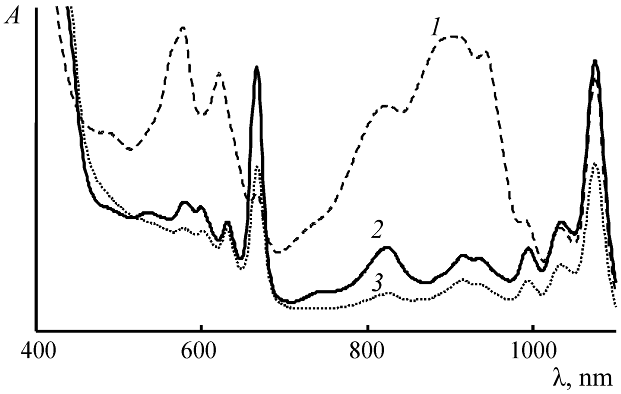


Fig. 4. EAS of the reaction mixture in the reaction of C_{60} with $PcSi(OH)_2$ (2:1) in the presence of KOH in THF and 15C5: 24 h (*1*) and after contact with atmospheric O_2 for 5 min (*2*) and 20 min (*3*). The reaction was performed in an evacuated cell.

after exposure to O_2 or atmospheric O_2 for 10–15 min (Fig. 4). This result is consistent with the low basicity of C_{60}^{-} well-known from the literature [17]. The reaction of C_{60}^{-} with CF_3COOH leads to full extinguishing of the absorption bands of C_{60}^{-}, therewith regeneration of the absorption bands of the original $PcSi(OH)_2$ does not occur (Fig. 2).

Reactions of C_{60}^{2-} with CF_3COOH and O_2. CF_3COOH instantly reacts with the C_{60}^{2-}, extinguishing the absorption in the region of 800–1000 nm. The spectrum of the reaction mixture in the visible region, as well as the color of the reaction mixture, change very little, SiPc is not formed in the reaction of C_{60}^{2-} with CF_3COOH (Fig. 3). Changes in the spectrum of C_{60}^{2-} in the course of reaction with O_2 are almost the same: the absorption in the near infrared region disappears, in the visible area the changes are minor. It is obvious that in general the reactions of C_{60}^{2-} with H^+ or O_2 are the neutralization of the C_{60}^{2-} charge either by electron transfer to oxygen to form superoxide anion O^{2-}, or through the fullerene protonation. In both cases, this means irreversible loss of electrons donated by silicon phthalocyanine to the fullerene and leads to the inevitable degradation of the phthalocyanine. In the dianion Pc^{2-} obtained by an intramolecular rearrangement, as in the D–A complexes of silicon phthalocyanine, the phthalocyanine structure of the original environment is restored after neutralization of the proton donor [7].

Spectral analysis of the C_{60}^{-} and C_{60}^{2-} fullerides. In the ^1H NMR spectra of the fullerides of C_{60}^{-} and C_{60}^{2-} there is a single signal at the δ 7.25 ppm. In the ^1H NMR spectra of the C_{60}^{2-} fulleride three groups of the signals of aromatic protons can be isolated: (1) δ 7.80–7.70 ppm, (2) δ 7.60–7.50 ppm, (3) δ 7.40–7.10 ppm. They all correspond to the four protons of the benzoid fragments of the phthalocyanine structure forming a cation counterpart of the C_{60}^{2-} fulleride. The ^1H NMR spectra of the C_{60}^{2-} are practically identical to those of the D–A complexes of SiPc in DMSO obtained in [7], where it has been shown that the first group of protons (δ 8.20–7.80 ppm) belongs to benzoid fragment of the acceptor (that is, $PcSiH_2$) in the D–A complex. After the interaction with O_2, this group disappears from the ^1H NMR spectrum for $PcSiH_2$ is displaced from the D–A complex by oxygen. Similarly, after the reaction of C_{60}^{2-} with O_2 the signals of the first group disappear from the ^1H NMR spectrum. Obviously, the first group of protons with the δ 7.80–7.70 ppm belongs to the D–A (**II**) complex formed in the synthesis of fulleride C_{60}^{2-}. In the reaction with a ratio of $C_{60}/PcSi(OH)_2$ = 3:1 by increasing reaction time we succeeded to get C_{60}^{2-} with an admixture of the D–A complex not exceeding 10%, and it falls to zero after the reaction with O_2.

The data of ESR spectra of C_{60}^{-} in xylene: g_i = 1.9999, ΔH = 1.25 Oe; in THF: (a) 1. g_i = 2.0012, ΔH ~7.62 Oe, 2. g_i = 1.9999, ΔH = 1.28 Oe ; (b) g_i = 1.9999, ΔH = 1.20 Oe. C_{60}^{2-} in DMSO: 1. g_i = 2.0000, ΔH = 0.18 Oe ; 2. $g_{\|}$ = 1.9996, $g_{\perp}$ = 2.00043.

The IR spectra of fullerides C_{60}^{-} and C_{60}^{2-} are poorly informative, since the bands are almost completely covered by intense absorption bands of crown ether 15C5 or DMSO, which are coordinated with the fulleride.

Thus, the silicon phthalocyanine dianions obtained at the silicon phthalocyanine dihydroxide rearrangement in an alkaline medium reduce the fullerene C_{60} to C_{60}^{-} monoanion and C_{60}^{2-} dianion, and through oxidation to the dication form with them ionic compounds, the fullerides C_{60}^{-} or C_{60}^{2-}. The fullerides are stable at room temperature, but, when exposed to oxygen or a proton donor, they are destroyed irreversibly, and the original phthalocyanine structures are not regenerated. We obtained a further evidence of the surprizing mobility of the electronic system of silicon phthalocyanine, which is rearranged in the dianion at the expense of the two electrons from the axial oxygen atoms, and then passes this pair of electrons to the molecules of fullerene C_{60}. Apparently, such a rearrangement of the electron system of phthalocyanine silicon is observed for the first time.

EXPERIMENTAL

$PcSi(OH)_2$ was prepared according to the procedure in [22].

Toluene and THF were distilled and stored over sodium-benzophenone ketyl and dosed by condensation in a vacuum, *o*-xylene was dried and distilled over Na, DMSO was dried over Na_2SO_4 and distilled in a vacuum. In this work we used KOH of chemically pure grade. Oxygen O_2 was obtained by thermal decomposition of $KMnO_4$.

The silicon phthalocyanine dianion (Pc^{2-}) was obtained in the reaction of $PcSi(OH)_2$ with KOH or NaOH in the presence of crown ether 15C5 in xylene at 50–150°C. The reaction was performed in the absence of air, with removal from time to time of the evolved H_2O in a vacuum with small amounts of xylene or toluene. The interaction with Pc^{2-} with C_{60} was performed in the absence of air in the optical cell at room temperature with stirring the reaction mixture with a magnetic stirrer. A solution of C_{60} in toluene was poured to the Pc^{2-} solution. In this case the reaction proceeded in the presence of solid alkali. In some experiments, on the contrary, a solution of Pc^{2-} in xylene or toluene was poured to a solution of C_{60}, in this case the reaction was carried out in the absence of a solid alkali.

In most experiments, to obtain the C_{60}^{-} or C_{60}^{2-} a reaction of C_{60} with $PcSi(OH)_2$ was carried out in xylene or THF in the presence of KOH with the addition of crown ether 15C5, or in DMSO without the crown ether. We used either solid alkali, which was the reagent and the absorber of H_2O released in the reaction, or the KOH in a complex with 15C5 or in solution in DMSO. The reactions were performed at 20±2°C in evacuated ampules, sealed to an optical cell and a tube for the measurement of ESR or NMR spectra. In one experiment 1–10 mg of $PcSi(OH)_2$, 5–20 mg of KOH, 10–20 ml of either xylene, or THF, or DMSO were used. Some experiments were performed in cells with 0.2–0.5 mg of $PcSi(OH)_2$, 5–10 mg of KOH, and 5 ml of either xylene, or THF, or DMSO. As the color changed, the absorption spectra of the reaction mixture were measured in the UV, visible and near-IR regions, and ESR or ^1H NMR spectra, which were correlated with the corresponding absorption spectra.

The EAS were recorded on a Perkin Elmer Lambda 25 spectrometer, ^1H NMR spectra, on a Bruker DPX 200 spectrometer; ESR spectra, on a Bruker EMX-8/2.7 instrument of the Analytical Center of the Institute of Organometallic Chemistry, Russian Academy of Sciences.

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