

New complexes of fullerenes C₆₀ and C₇₀ with Co^{II} and Mn^{II} tetraphenylporphyrinates and their ESR study

E. I. Yudanov,*, D. V. Konarev, L. L. Gumanov, and R. N. Lyubovskaya

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588. E-mail: yudan@icp.ac.ru

Complexes of fullerenes C₆₀ and C₇₀ with cobalt(II) and manganese(II) tetraphenylporphyrinates of compositions Mn(TPP)·(C₆₀)₂(CS₂)_{1.5} (1), Mn(TPP)·C₇₀(CS₂)_x, where $x \leq 1.25$ (2), Co(TPP)·C₆₀(CS₂)_{0.5} (3), and Co(TPP)·C₇₀(CS₂)_x, where $x < 0.25$ (4), were synthesized and studied by ESR spectroscopy. At 77 K, complexes 1 and 2 have singlet ESR spectra characteristic of the low-spin ($S = 1/2$) state of Mn^{II}, with $g = 2.002$ and linewidths of 250 G and 300 G, respectively, and differing significantly from that of the initial Mn^{II}(TPP) ($g_{\perp} = 5.9$ and $g_{\parallel} = 2.0$, $S = 5/2$). The spectra of complexes 1 and 2 exposed to oxygen exhibit hyperfine structure due to interaction with ⁵⁵Mn and ¹⁴N nuclei. The ESR spectra of complexes 3 and 4 are asymmetric ($\langle g \rangle = 2.4$, $\Delta H_{pp} = (500-600)$ G), which is due to the overlap of parallel and perpendicular spectral components. The absence of ESR signals from C₆₀^{·-} and C₇₀^{·-} radical anions makes it possible to conclude that the formation of complexes 1-4 is not accompanied by electron transfer from Co(TPP) and Mn(TPP) to fullerenes C₆₀ and C₇₀.

Key words: fullerenes C₆₀ and C₇₀, Co^{II} tetraphenylporphyrinate and Mn^{II} tetraphenylporphyrinate, synthesis, ESR spectroscopy.

It is known that fullerenes exhibit acceptor properties and form donor-acceptor compounds with organic and organometallic donors.¹⁻⁸ Because of weak acceptor properties of fullerenes ($E_{ox}(C_{60}) = -0.44$ V, $E_{ox}(C_{70}) = -0.41$ V vs. s.c.e in dichloromethane⁹) and steric peculiarities of their molecules, most fullerene compounds are characterized by weak charge transfer from donor to fullerene.⁶⁻⁸ Only several compounds are capable of reducing fullerenes to radical anions without side addition reactions: tetrakis(dimethylamino)ethylene (TDAE),¹ several metallocenes,^{2,3} and substituted metalloporphyrins, viz., chromium tetraphenylporphyrinate, Cr(TPP) ($E_{ox} = -0.86$ V),⁴ and tin tetra-*p*-tolylporphyrinate, Sn(TpTP) ($E_{ox} = -1.17$ V).⁵ In a toluene-THF mixture the Cr(TPP) complex reduces fullerene C₆₀ to form the Cr(TPP)·C₆₀(THF)₃ salt characterized by an ESR signal corresponding to C₆₀^{·-}.⁴ This reduction is reversible and the equilibrium is shifted toward the formation of neutral C₆₀ in neat toluene.⁴ In the presence of *N*-methylimidazole (*N*-MeIm), fullerene C₆₀ reacts with Sn^I(TpTP) to give the Sn(TpTP)(*N*-MeIm)₂(C₆₀)₂ salt.⁵

Currently, intensive studies are carried out on complexes between metalloporphyrins and planar π -acceptors, since many of them exhibit interesting magnetic properties. For instance, manganese tetraphenylporphyrinate reacts with tetracyanoethylene and other acceptors to give salts which are one-dimensional ferromagnetics at liquid helium temperature.¹⁰ Fullerenes also

exhibit the properties of π -acceptors, have spherical molecules, and can be coordinated to porphyrins containing mobile aromatic substituents.

In this work, we report the synthesis of new complexes of fullerenes C₆₀ and C₇₀ with organometallic donors, viz., tetraphenyl-substituted cobalt(II) and manganese(II) porphyrinates (Co(TPP) and Mn(TPP), respectively), and the study of their electronic state by ESR spectroscopy. Compounds Co(TPP) and Mn(TPP) are rather strong donors: $E_{ox}(\text{Co(TPP)}) = +0.52$ V in benzonitrile¹¹ and $E_{ox}(\text{Mn(TPP)}) = -0.23$ V in acetonitrile¹² (both vs. s.c.e). For Co(TPP), the ground spin state is the low-spin ($S = 1/2$) state,¹³ whereas for Mn(TPP) it is the high-spin ($S = 5/2$) state.¹⁴ Since the difference in the redox potentials between Mn(TPP) and fullerenes is small (0.18 to 0.21 V),^{9,12} one could expect that the reaction of C₆₀ and C₇₀ with Mn(TPP) will result in complexes with considerable charge transfer. The obtained complexes were studied by ESR spectroscopy, which is the method most sensitive to a change in the electronic state of metalloporphyrins and fullerenes in complexes.

Experimental

The Co(TPP) and Mn(TPP) complexes were synthesized using fullerenes C₆₀ and C₇₀ of purity 99.9% and 98%, respectively, following the known procedures.^{11,12} The data of elemental analysis as well as the ESR and IR spectra of the

metalloporphyrins coincided with the reported data.^{11–14} Carbon disulfide and ether were distilled under an argon atmosphere immediately prior to use. To obtain the complexes, equimolar solutions of C_{60} or C_{70} and Mn(TPP) or Co(TPP) in carbon disulfide were filtered and evaporated in an argon box over 6 to 12 days. Since Mn(TPP) in the complexes with fullerenes is unstable to oxidation, all operations with this compound were carried out in an argon atmosphere. The crystals obtained (lengthened parallelepipeds with a specific blue luster) were washed with ether until complete decoloration of the initial metalloporphyrin and dried. The yields of complexes with respect to fullerene amounted to 50%. Complexes with Co(TPP) are stable in air. In addition to the complexes, a $C_{60}(CS_2)_x$ crystal solvate was obtained in the reaction as lengthened black plates. Crystals for elemental and thermogravimetric analyses were separated from the crystal solvate under a microscope. The following compositions of the complexes were established from the data of elemental analysis: Mn(TPP) · $C_{60}(CS_2)_{1.5}$ (1), Mn(TPP) · $C_{70}(CS_2)_x$ ($x \leq 1.25$) (2), Co(TPP) · $C_{60}(CS_2)_{0.5}$ (3), and Co(TPP) · $C_{70}(CS_2)_x$ ($x \leq 0.25$) (4) (Table 1).

The content of solvent in complexes 1 and 3 was confirmed by thermogravimetric analysis. For compound 1 the mass loss associated with removal of CS_2 was 5.1% at 453 K, which is close to the content of CS_2 according to the data of elemental

analysis (4.55%). For compound 3 the loss of CS_2 at 473 K was 3.0% (1.61% according to the data of elemental analysis).

The ESR spectra were recorded at 77 and 300 K on a Radiopan SE/X-2547 spectrometer operating at a magnetic modulation frequency of 100 kHz and equipped with an MCM101 nuclear magnetometer and a wavemeter. To minimize the time of contact of the crystals with air, the crystals were placed into the ESR ampules immediately after the preparation; because of this, the specimens of complexes 1–4 could contain an admixture of $C_{60}(CS_2)_x$, which exhibits no ESR signals.

The ESR spectra of initial donor compounds Mn(TPP) and Co(TPP) at 77 K are shown in Fig. 1 and coincide with the reported data.^{13,14} Manganese tetraphenylporphyrinate is a high-spin complex characterized by ESR spectrum with g -factor anisotropy ($g_{\perp} = 5.9$, $g_{\parallel} = 2.0$) and hyperfine structure (HFS) due to the interaction with ^{55}Mn nuclei (spin $I = 5/2$). Since the spin concentration in the Mn(TPP) specimens used was high, no hyperfine interaction (HFI) with ^{55}Mn nuclei was observed. The low-spin Co(TPP) complex has an ESR spectrum with resolved HFS and g -factor anisotropy (^{59}Co , $I = 7/2$, $g_{\perp} = 3.322$, $B = 395 \cdot 10^{-4} \text{ cm}^{-1}$, $g_{\parallel} = 1.798$, $A = 197 \cdot 10^{-4} \text{ cm}^{-1}$).¹³ Exposure of the specimen to oxygen causes the appearance of additional spectral lines due to the formation of a second Co^{2+} center in the Co(TPP) complex. As previously, the ESR spectrum of Co(TPP) was not observed at room temperature because of a short relaxation time.¹³

Table 1. Data of elemental analysis for complexes 1–4

Complex	Found / Calculated (%)			
	C	H	N	S
Mn(TPP) · $C_{60}(CS_2)_{1.5}$ (1) ^a	91.08 89.48	1.25 1.25	2.21 2.51	4.55 4.30
Mn(TPP) · $C_{70}(CS_2)_x$, $x \leq 1.25$ (2) ^b	85.14 86.41	2.14 1.74	3.68 3.47	4.86 4.96
Co(TPP) · $C_{60}(CS_2)_{0.5}$ (3) ^c	89.41 87.93	1.89 1.95	4.03 3.78	1.61 2.22
Co(TPP) · $C_{70}(CS_2)_x$, $x \leq 0.25$ (4) ^d	90.15 89.66	2.12 1.82	3.76 3.64	0.98 1.04

^a Calculated (%): Mn, 2.46.

^b Calculated (%): Mn, 3.42.

^c Calculated (%): Co, 4.12.

^d Calculated (%): Co, 3.84.

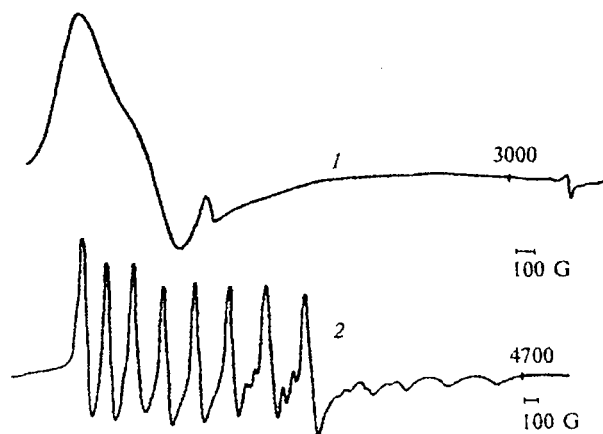


Fig. 1. ESR spectra of initial donor compounds ($T = 77 \text{ K}$): 1, Mn(TPP); 2, Co(TPP).

Results and Discussion

The ESR spectra of complexes 1 and 2 in an argon atmosphere at 77 K (Fig. 2, spectrum 1) are superpositions of a broad line ($g = 2.002$, $\Delta H_{pp} = 250 \text{ G}$; and 2: $g = 2.002$, $\Delta H_{pp} = 300 \text{ G}$) and a narrow signal ($g_{\perp} = 2.0022$ and $\Delta H_{pp, \perp} = 1.5 \text{ G}$ for both compounds). The latter is observed in all spectra of the complexes of C_{60}

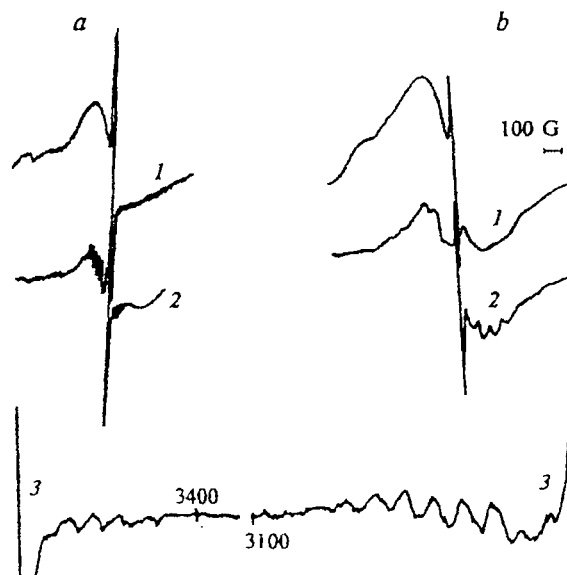


Fig. 2. ESR spectra of complexes 1 (a) and 2 (b) at 77 K: 1, in argon atmosphere; 2, 10 min after exposure to air; and 3, a 400 G region of the spectrum of complex 2.

and C_{70} as well as in those of the initial fullerene powders. According to the reported data,¹⁵ this signal is due to defects caused by the interaction between fullerenes and oxygen, the concentration of defects being equal to 10^{-4} to 10^{-5} mol L^{-1} . The signal intensity depends on the procedure of preparation and purification of fullerenes and on the duration of exposure of fullerene to air (especially on heating). We will not consider this signal below.

Exposure of specimens 1 and 2 to air for 10 min leads to the appearance of HFS in the ESR spectra, which is due to interaction between the unpaired electron with the nuclei of nitrogen atoms ($I = 1$) of the pyrrole ring of TPP in complex 1 (thirteen weak lines with intervals A of 17.5 G between them and ΔH_{pp} values of 8 G) and with the ^{55}Mn nuclei in complex 2 (six lines with intervals A_1 of 83 G between them) (Fig. 2, spectra 2, 3). We believe that two additional HFS components in the spectrum of complex 1 are indistinguishable against the background of the central spectral component. Exposure of the specimens to oxygen for several hours leads to disappearance of the ESR spectra of the complexes and only the narrow signal is observed. The values of g -factors of complexes obtained are characteristic of the low-spin ($S = 1/2$) state of $\text{Mn}(\text{TPP})$. In the air, $\text{Mn}^{\text{II}}(\text{TPP})$ reacts with oxygen and is oxidized to give the diamagnetic $\text{Mn}^{\text{III}}(\text{TPP})$. In this case a local decrease in the Mn^{II} concentration in the complexes occurs initially and, hence, the exchange and dipole-dipole interactions between neighboring spins weaken, which favors the manifestation of HFS due to the interaction with paramagnetic ^{55}Mn and ^{14}N nuclei.

A substantial overlap of the spin orbitals of $\text{Mn}(\text{TPP})$ with π -orbitals of fullerenes C_{60} and C_{70} in the complexes obtained causes appreciable changes in ESR spectra of the complex with $\text{Mn}(\text{TPP})$. The distinctions in the type of these interactions should be pointed out. In complex 2 the unpaired electron is localized mainly on d -orbitals of the Mn atom and interacts with its nucleus, which results in the appearance of HFS components. In this case no HFS due to interaction with the ^{14}N nuclei of the pyrrole ring nitrogens is observed. In complex 1 the unpaired electron is localized mainly on the pyrrole ring orbitals, since no HFI with the ^{55}Mn nuclei is observed. This indicates that d -orbitals of the Mn atom and the pyrrole ring nitrogens in complex 1 are strongly coupled.

Such a distinction in the ESR spectra of complexes 1 and 2 can be explained by different crystal structure and composition of these complexes. In the unit cell of complex 1 manganese tetraphenylporphyrinate interacts with two fullerene molecules, whereas in the unit cell of complex 2 it interacts with one fullerene molecule. According to calculations,¹³ organometallic square-bonded complexes such as $\text{Co}(\text{TPP})$, $\text{VO}(\text{TPP})$, and $\text{Cu}(\text{TPP})$ are characterized by strong σ -bonding and very weak π -bonding in the pyrrole ring plane. π -Bonding out of this plane is strong for Co and VO complexes and weak

for Cu complexes; because of this, HFS due to interaction with both Cu atomic nuclei and ^{14}N nuclei is observed in the ESR spectra of $\text{Cu}(\text{TPP})$.¹³ By analogy, it can be assumed that for complex 1 the HFS is due to both interaction with ^{14}N nuclei and weakening of the π -bonding out of the pyrrole ring plane of TPP because of interaction with fullerene C_{60} orbitals. If C_{60} molecules form a symmetric environment of $\text{Mn}(\text{TPP})$, the interaction of fullerene orbitals with those of the pyrrole ring is stronger than with d -orbitals of the Mn^{2+} ion, and the unpaired electron is localized mainly on the orbitals of N atoms. In complex 2, for one $\text{Mn}(\text{TPP})$ molecule there is one C_{70} molecule; for this reason, it is likely that $\text{Mn}(\text{TPP})$ and C_{70} are packed more loosely, which causes weaker perturbations of $\text{Mn}(\text{TPP})$ orbitals. In this complex the unpaired electron is localized mainly on the orbitals of the Mn atom. In addition, the spherical shape of the C_{60} molecule is sterically more preferable for coordination to $\text{Mn}(\text{TPP})$ than the ellipsoidal shape of fullerenes C_{70} , which provides a rather strong interaction in C_{60} complexes. More precise information on local interactions between Mn and fullerenes C_{60} and C_{70} can be obtained from X-ray analysis data.

The ESR spectra of complexes 3 and 4 at $T = 77$ K are shown in Fig. 3 (spectra 1, 3). In contrast to the initial $\text{Co}(\text{TPP})$, the ESR spectra of these complexes are observed even at room temperature. Both complexes are characterized by a broad intense asymmetric line with $\langle g \rangle = 2.4$ and $\Delta H_{pp} = 500$ – 600 G, which is a result of the overlap of parallel and perpendicular components of the spectrum of a polycrystalline specimen. An 8-component spectrum due to HFI with ^{59}Co nuclei ($I = 7/2$) with a separation of 170 G between the components is also observed against the background of the broad line.

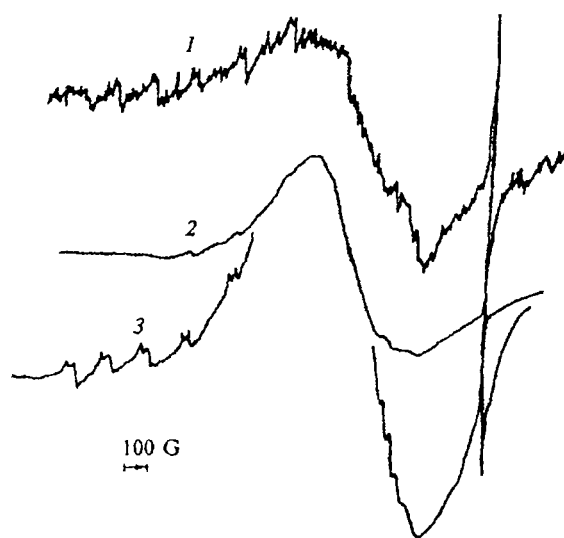


Fig. 3. ESR spectra of complexes 3 and 4 ($T = 77$ K): 1, complex 3, amplification $5 \cdot 10^3$; 2, complex 4, amplification $5 \cdot 10^2$; and 3, complex 4, amplification $5 \cdot 10^3$.

Each line is additionally split into HFS components separated by intervals of 17 to 18 G, which is due to HFI with N atoms. The intensities of the latter lines are two orders of magnitude lower than that of the main spectral line. Possibly, this signal is due to the unreacted initial Co^{II}(TPP).

The interaction between fullerene and Co(TPP) orbitals in complexes **3** and **4** is weaker than that between fullerene and Mn(TPP) orbitals in complexes **1** and **2**. The ESR spectra of Co(TPP) in complexes **3** and **4** also correspond to the low-spin state and are characterized by *g*-factor anisotropy (only their numerical values are changed), and the type of interaction with fullerenes in complexes **3** and **4** is likely the same. Changes in the ESR spectrum characteristic of Co(TPP) observed for **3** and **4** are first of all due to a decrease in the HFI constants *A* and *B* that are very sensitive to local interactions.

It is most likely that no electron transfer from the metal atoms of Co(TPP) and Mn(TPP) fragments to C₆₀ or C₇₀ occurs at the formation of complexes **1**–**4**. It is known that Mn(TPP) is a strong donor toward C₆₀ and C₇₀ (the *E*_{ox} values in acetonitrile are –0.23,¹² –0.44, and –0.41 V, respectively, all vs. s.c.e.) and that the difference in the redox potentials ($\Delta E = 0.18$ – 0.21 V) is sufficient to form complexes with considerable charge transfer. Presumably, the observed absence of charge transfer in Mn(TPP) complexes is due to their formation in the nonpolar solvent (CS₂), which substantially decreases the redox potential of the Mn^{II}(TPP)/Mn^{III}(TPP) pair relative to the C₆₀/C₆₀^{•–} or C₇₀/C₇₀^{•–} pairs whose redox potentials are slightly dependent on the solvent polarity. An analogous situation is observed⁴ in the case of reaction between a strong organometallic donor Cr(TPP) and C₆₀. Cobalt^{II} tetraphenylporphyrinate is a weak donor toward fullerene (*E*_{ox} = +0.52 V vs. s.c.e. in benzonitrile)¹¹ even in polar solvents; for this reason, only a molecular complex can be formed in this case.

The results obtained suggest that the strongest interaction and the largest overlap of π -orbitals of fullerenes and organometallic donors Mn(TPP) and Co(TPP) at the formation of complexes **1**–**4** is observed for complexes **1** and **2** and that the type of Mn(TPP) coordination to C₆₀ and C₇₀ may be different. In both complexes **1** and **2**, Mn(TPP) is in the low-spin state (*S* = 1/2).

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