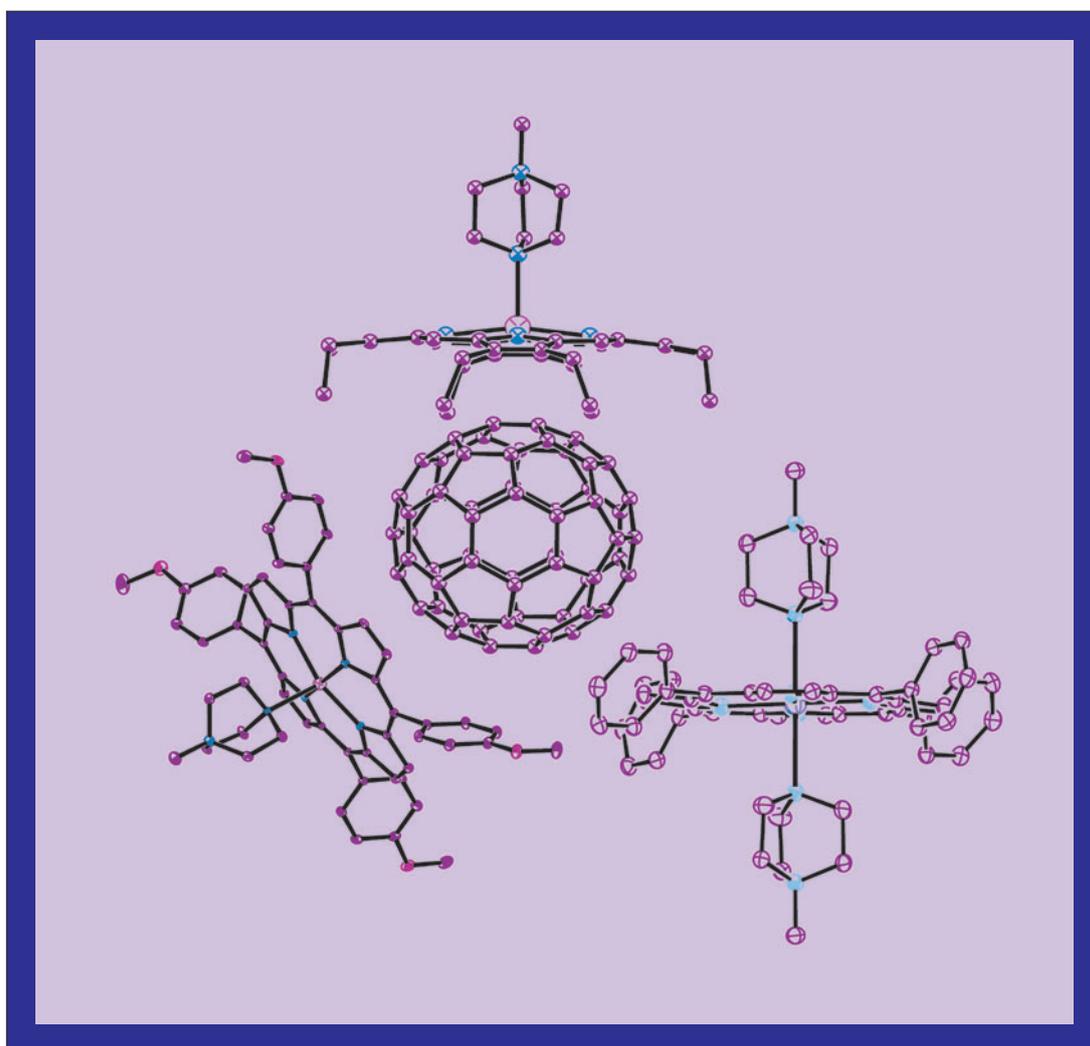


Coordination Structures of Metalloporphyrins with *N*-Containing Cations in Complexes with Fullerenes

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Ionic complexes of fullerenes with metalloporphyrins attract much attention due to promising photophysical and magnetic properties. We design these complexes using the coordination bonding between metalloporphyrins and N-containing cations (M-N(L⁺) bonds). In this review we discuss 1). C₆₀^{•-}, C₆₀²⁻ and C₇₀⁻ complexes with (MDABCO⁺)₂·M^{II}TPP units (MDABCO⁺ is N-methyldiazabicyclooctane cation, M = Zn, Co, Mn, Fe, **1-6**) having six-coordinated metal centres; 2). C₆₀⁻ complexes with (MDABCO⁺)·M^{II}TMPP (M = Zn (**7**), Co (**8**)) and (MDABCO⁺)·M^{II}OEP units (M = Zn, Co, Mn, Fe, **9-12**) having five-coordinated metal centres. We discuss synthesis of the complexes, structures of metalloporphyrins coordinatively bound with N-containing cations formed in the complexes with fullerenes, and the magnetic properties of the complexes.

Keywords: Octaethyl- and tetraphenylporphyrins, complexes, fullerenes, coordination.

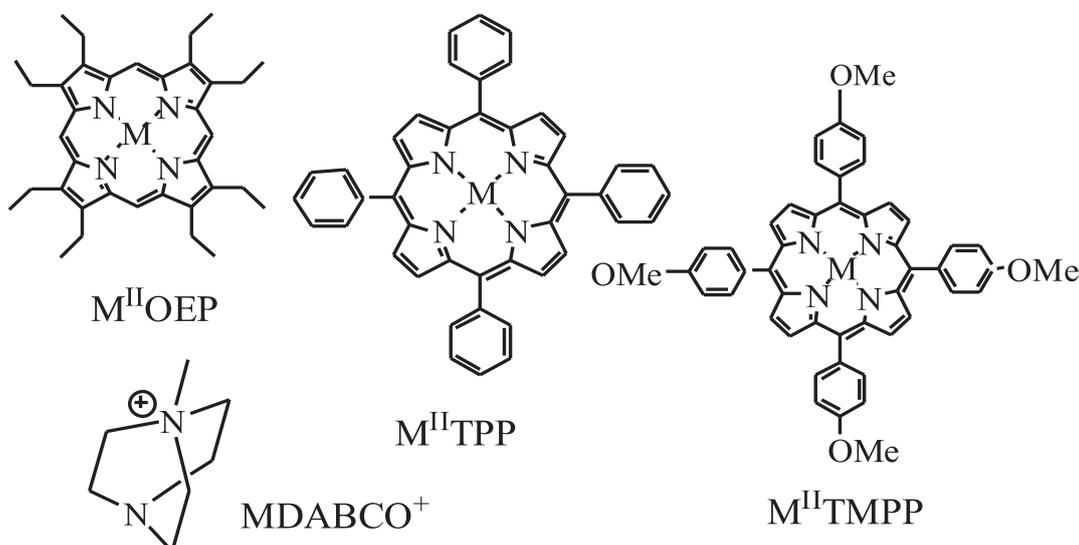
Introduction

Fullerenes form variety of molecular and ionic complexes with metalloporphyrins.^[1-6] These complexes attract much attention since porphyrin molecules are able to form complexes not only with fullerenes but with variety of endometallofullerenes and chemically modified fullerenes.^[1,7-9] That allows to investigate the molecular and electronic structures of new fullerene families. Design of ionic complexes of fullerenes and metalloporphyrins is a promising approach to study fullerenes in a charged state including anions of endometallofullerenes and chemically modified fullerenes. The other interesting possibility of this approach is the preparation and study of new σ-bonded structures from negatively charged fullerenes. Since fullerene

anions have strong tendency for dimerization, polymerization or coordination lead to the new types of fullerene dimers, polymers and coordinatively bound units.^[10]

Since fullerenes are relatively weak acceptors (in compare with planar π-acceptors tetracyanoethylene or tetracyanoquinodimethane)^[11] most of fullerene complexes with metalloporphyrins have only neutral ground state.^[1-5] We developed new approach for the preparation of ionic fullerene-porphyrin complexes which uses the relatively weak coordination bonding between metalloporphyrins and N-containing cations (the M-N(L⁺) bonds).^[12-17]

For example, N-methyldiazabicyclooctane cation (MDABCO⁺, Scheme 1) has a free nitrogen atom capable to coordinate to different metalloporphyrins. Since MDABCO⁺ can be a counter cation for the fullerene anions, neutral



Scheme 1.

metalloporphyrin molecules are involved into the ionic complexes with fullerenes in form of positively charged coordination assemblies: $\{(MDABCO^+) \cdot M^{II}porphyrin\} \cdot (C_{60}^-)_n$ ($n = 1$ and 2). This approach allows to obtain ionic supramolecular complexes with fullerenes containing diamagnetic singly bonded $(C_{70}^-)_2$ dimers in $\{(MDABCO^+) \cdot Mn^{II}TPP\} \cdot \{(MDABCO^+) \cdot \{(C_{70}^-)_2\}_2 \cdot (Solvent)_x$ (TPP is tetraphenylporphyrin, Scheme 1)^[12] as well as unusual $(C_{60}^-)_2$ dimers bonded by two single bonds having biradical state at room temperature in $\{(MDABCO^+) \cdot M^{II}TMPP\}_2 \cdot (C_{60}^-)_2 \cdot (Solvent)_x$ ($M = Co^{II}, Zn$; TMPP is tetrakis(4-methoxyphenyl) porphyrin, Scheme 1).^[13,14] Fullerene anions can also preserve the monomeric state in the complexes forming antiferromagnetically coupled $C_{60}^{\bullet-}$ chains in $\{(MDABCO^+) \cdot M^{II}TPP\} \cdot (C_{60}^-)_2 \cdot (Solvent)_x$ ^[12] and $\{(MDABCO^+) \cdot M^{II}OEP\} \cdot (C_{60}^-)_2 \cdot (Solvent)_x$ complexes ($M = Zn, Co, Mn$, and Fe)^[15,16] (OEP is octaethylporphyrin, Scheme 1). Recently it was shown that not only fullerene radical anions but fullerene dianions can be involved into the ionic complexes with the coordination assemblies of metalloporphyrins allowing to study the electronic state of more negatively charged fullerenes.^[17] The supposed method of synthesis provides interesting possibility to study the coordination assemblies of metalloporphyrins with the coordination cations as well. This field of coordination chemistry of metalloporphyrins is not well studied

In this review we discuss synthesis, structures and magnetic properties of the ionic complexes of fullerenes and metalloporphyrins coordinated by *N*-containing cations.

Results and Discussion

$C_{60}^{\bullet-}, C_{60}^{2-}$ and C_{70}^- complexes with $(MDABCO^+) \cdot M^{II}TPP$ units (**1-6**)

To prepare **1-5** we used the reduction of fullerenes with CH_3CH_2SNa in the presence of MDABCO-I excess in $C_6H_4Cl_2/C_6H_5CN$ (19:1) mixture. Then $(MDABCO^+) \cdot (fullerene^{\bullet-})$ salt was precipitated from the solution by hexane in the presence

of corresponding metalloporphyrin. The coordination of MDABCO⁺ to metalloporphyrin is a key point for the formation of **1-5** since copper(II) tetraphenylporphyrin which can not coordinate MDABCO⁺ does not form such complexes. For preparation of **6** an excess of CH_3CH_2SNa , MDABCO-I and C_{60} were stirred in acetonitrile (CH_3CN). The reduction occurred up to -2 charged state (according to the NIR spectra) and was accompanied by the cationic metathesis reaction. The addition of *o*-dichlorobenzene ($C_6H_4Cl_2$) and $Mn^{II}TPP$ with further diffusion of hexane into the obtained solution yielded the crystals of **6**. The compositions of **1-6** are listed in Table 1. The compositions of **1** and **4** were determined from elemental analyses and those of **2, 3, 5** and **6** from X-ray structural analysis. The compositions of **1-4** are similar and differ only in the content of solvent molecules: $\{(MDABCO)_2 \cdot M^{II}TPP\} \cdot (C_{60}^-)_2 \cdot (C_6H_4Cl_2)_{2.2+x} \cdot (C_6H_5CN)_y$ ($x = 0 - 2.2$, $y = 0 - 1.8$). Therefore, all these complexes most probably contain the same $(MDABCO^+) \cdot M^{II}TPP$ units and fullerene anions at 1:2 molar ratio. **5** has a composition of another character and involves free non-coordinated MDABCO⁺ cations additionally to $(MDABCO^+) \cdot Mn^{II}TPP$ units.

Metalloporphyrins coordinate two MDABCO⁺ cations in both **2** and **3**. Therefore, metal atoms are six-coordinated and have the octahedral environment at M^{II} centres ($M = Co$ (Figure 1a) and Mn). Previously such environment was reported for $Co^{II}TPP$ in $(piperidine)_2 \cdot Co^{II}TPP$ ^[18] and by our knowledge was for the first time found for $Mn^{II}TPP$ since even in a large excess of *N*-containing ligands such as pyridine and imidazole (L), $Mn^{II}TPP$ forms only five-coordinated $L \cdot Mn^{II}TPP$ species.^[19] Most probably, crystal packing forces in the complex with fullerene facilitate the stabilization of six-coordinated metalloporphyrins. The $Co \cdots N(MDABCO^+)$ distances of 2.475(2) and 2.553(2) Å indicate weak coordination of MDABCO⁺ to metalloporphyrins. The elongation of Co-N axial coordination bonds from 2.157(3) to 2.436(2) Å was observed when moving from five-coordinated (imidazole)- $Co^{II}TPP$ to six-coordinated $(piperidine)_2 \cdot Co^{II}TPP$. This elongation is a consequence of that an unpaired electron involved in the bonding is located on

Table 1. Composition of the complexes.

N	Complex	Ref.
1	$\{(MDABCO)_2 \cdot ZnTPP\} \cdot (C_{60}^-)_2 \cdot (C_6H_4Cl_2)_{2.5} \cdot (C_6H_5CN)_{0.5}$	[12]
2	$\{(MDABCO)_2 \cdot Co^{II}TPP\} \cdot (C_{60}^-)_2 \cdot (C_6H_4Cl_2)_{4.4} \cdot (C_6H_5CN)_{1.6}$	[12]
3	$\{(MDABCO)_2 \cdot Mn^{II}TPP\} \cdot (C_{60}^-)_2 \cdot (C_6H_4Cl_2)_{4.2} \cdot (C_6H_5CN)_{1.8}$	[12]
4	$\{(MDABCO)_2 \cdot Fe^{II}TPP\} \cdot (C_{60}^-)_2 \cdot (C_6H_4Cl_2)_{2.2} \cdot (C_6H_5CN)_{0.8}$	[12]
5	$\{(MDABCO)_2 \cdot Mn^{II}TPP\} \cdot (MDABCO)_2 \cdot \{(C_{70}^-)_2\}_2 \cdot (C_6H_4Cl_2)_6 \cdot (C_6H_5CN)_5$	[12]
6	$\{(MDABCO^+) \cdot Mn^{II}TPP\} \cdot (C_{60}^{2-}) \cdot C_6H_4Cl_2 \cdot (CH_3CN)_2$	[17]
7	$\{(MDABCO^+) \cdot Co^{II}TMPP\}_2 \cdot (C_{60}^-)_2 \cdot (C_6H_4Cl_2)_{2.5} \cdot (C_6H_5CN)_{1.5}$	[13]
8	$\{(MDABCO^+) \cdot ZnTMPP\}_2 \cdot (C_{60}^-)_2 \cdot (C_6H_4Cl_2)_{2.15} \cdot (C_6H_5CN)_{1.85}$	[14]
9	$\{(MDABCO^+) \cdot ZnOEP\} \cdot (C_{60}^{\bullet-}) \cdot (C_6H_5CN)_{0.75} \cdot (C_6H_4Cl_2)_{0.25}$	[16]
10	$\{(MDABCO^+) \cdot Co^{II}OEP\} \cdot (C_{60}^{\bullet-}) \cdot (C_6H_5CN)_{0.67} \cdot (C_6H_4Cl_2)_{0.33}$	[15,16]
11	$\{(MDABCO^+) \cdot Fe^{II}OEP\} \cdot (C_{60}^{\bullet-}) \cdot (C_6H_5CN)_{0.4} \cdot (C_6H_4Cl_2)_{0.6}$	[16]
12	$\{(MDABCO^+) \cdot Mn^{II}OEP\} \cdot (C_{60}^{\bullet-}) \cdot (C_6H_5CN)_{0.88} \cdot (C_6H_4Cl_2)_{0.12}$	[16]

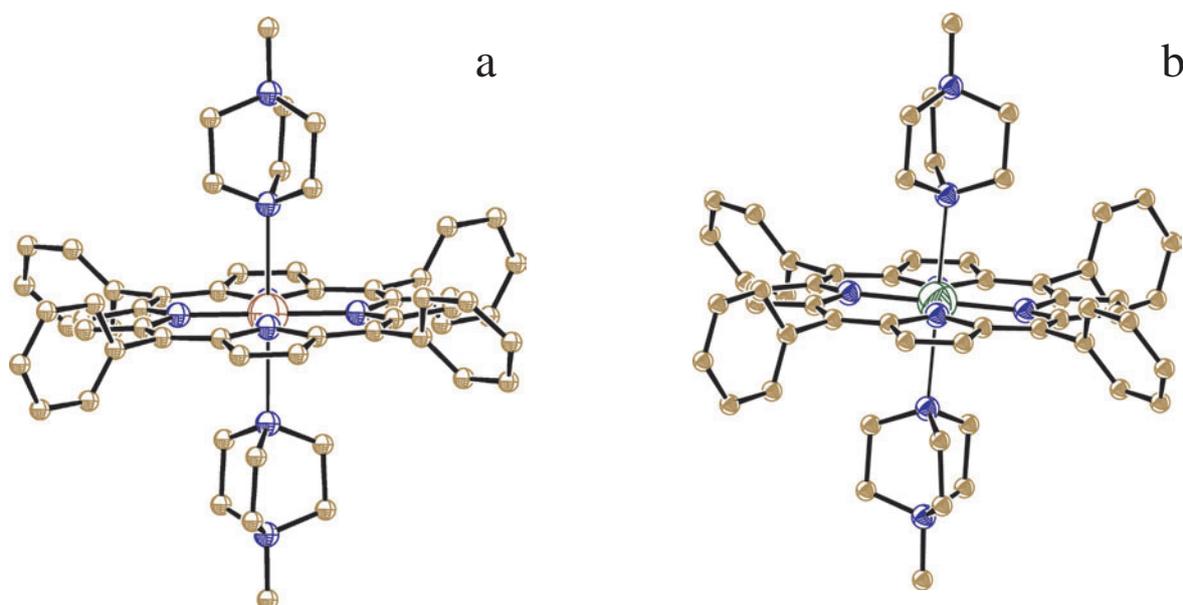


Figure 1. Coordination units formed with cobalt(II) and manganese(II) tetraphenylporphyrins: (a) $(\text{MDABCO}^+)_2 \cdot \text{Co}^{\text{II}}\text{TPP}$ in **2** and (b) $(\text{MDABCO}^+)_2 \cdot \text{Mn}^{\text{II}}\text{TPP}$ in **5**.^[12]

d_{z^2} -orbital, which pointed directly to the two nitrogen atoms of axial ligands.^[18,20] The removal of the electron from d_{z^2} -orbital in $\text{Co}^{\text{III}}\text{TPP}^+$ leads to the noticeable shortening of axial Co-N bonds in $(\text{piperidine})_2 \cdot \text{Co}^{\text{III}}\text{TPP}^+$ to 2.060(3) Å.^[21] For the same reason, the Mn-N axial coordination bond elongates in the $(\text{MDABCO})_2 \cdot \text{Mn}^{\text{II}}\text{TPP}$ units. This implies that an unpaired electron of $\text{Mn}^{\text{II}}\text{TPP}$ involved in the bonding with MDABCO^+ should also localize on d_{z^2} -orbital. Additional contribution to the elongation of M-N bonds in $(\text{MDABCO}^+)_2 \cdot \text{M}^{\text{II}}\text{TPP}$ (M=Co and Mn) can provide the repulsion between two positive charges of MDABCO^+ cations. Porphyrin macrocycles are nearly planar with root mean square deviations (rms) of 0.033 and 0.064 Å for **2** and **3**. The cobalt atom is in the porphyrin plane with the averaged length of the equatorial Co-N bonds of 1.988(2) Å, what is close to that observed for six-coordinated $(\text{piperidine})_2 \cdot \text{Co}^{\text{II}}\text{TPP}$ (1.987(2) Å).^[18] The length of equatorial

Mn-N bonds is averaged in **3** at 2.096(2) Å and is close to that in high-spin ($S = 5/2$) $\text{Mn}^{\text{II}}\text{TPP} \cdot (\text{C}_6\text{H}_5\text{CH}_3)_2$ (2.084(2) Å)^[22].

The geometric parameters of $(\text{MDABCO})_2 \cdot \text{Mn}^{\text{II}}\text{TPP}$ units in **5** (Figure 1b) and **6** are nearly the same as those in **3**. Coordinated nitrogen atoms of two MDABCO^+ cations and metal atom lie along a straight line in **2**, **3**, **5** and **6**, which is nearly perpendicular to the porphyrin plane in **2** and **3** (88°) and forms an angle of 85° in **5** and 87.3° in **6**. In previously described $(\text{piperidine})_2 \cdot \text{Co}^{\text{II}}\text{TPP}$ this line forms an angle of about 89° with the porphyrin plane.^[18] The Mn-N(MDABCO^+) distances in **5** and **6** are long (Table 2) also indicating the essential destabilization of these coordination units. The averaged lengths of Mn-N equatorial bonds in **5** and **6** (Table 2) are close to those in **3** and high-spin $\text{Mn}^{\text{II}}\text{TPP} \cdot (\text{C}_6\text{H}_5\text{CH}_3)_2$.^[22] The elongation of Mn-N(TPP) bonds is associated with the singly occupied $d_{(x^2-y^2)}$ -orbital in

Table 2. Geometric parameters of six-coordinated $\text{Mn}^{\text{II}}\text{TPP}$ in high- and low-spin states.^[17]

Complex	M-N(TPP), Å	M-N(L), Å	Mn...C distances, difference, Å	Displacement of N atoms from the porphyrin plane, Å
$(\text{MDABCO}^+)_2 \cdot \text{Mn}^{\text{II}}\text{TPP} \cdot (\text{C}_{60}^{+})_2 \cdot \text{Solvent}$ (high-spin) ^[12]	2.081(2) - 2.110(2) Mn ^{II} displaces out of plane by ± 0.127 Å	2.531(2)	3.456(2) - 3.479(2) 0.023	0.063 - 0.122
$(\text{MDABCO}^+)_2 \cdot \text{Mn}^{\text{II}}\text{TPP} \cdot (\text{C}_{70}^{-})_4 \cdot (\text{MDABCO}^+)_2 \cdot \text{Solvent}$ (high-spin) ^[12]	2.097(2) - 2.098(2) Mn ^{II} in plane	2.515(2)	3.446(2) - 3.486(2) 0.040	0.117 - 0.125
$(\text{MDABCO}^+)_2 \cdot \text{Mn}^{\text{II}}\text{TPP} \cdot (\text{C}_{60}^{2-})_2 \cdot \text{Solvent}$ (high-spin) ^[17]	2.093(1) - 2.094(1) Mn ^{II} in plane	2.545(1)	3.449(3) - 3.469(3) 0.020	0.104 - 0.118
$(\text{MDABCO}^+)_2 \cdot \text{Mn}^{\text{II}}\text{TPP} \cdot (\text{C}_{60}^{2-})_2 \cdot \text{Solvent}$ (high-spin) ^[17]	2.095(1) - 2.098(1) Mn ^{II} in plane	2.537(1)	3.444(3) - 3.477(3) 0.033	0.076 - 0.133
$\text{Mn}^{\text{II}}\text{TPP} \cdot (\text{C}_6\text{H}_5\text{CH}_3)_2$ (high-spin) ^[22]	2.082(2) - 2.085(2) Mn ^{II} displaces out of plane by ± 0.177 Å	-	3.466(3)	0.030 - -0.140
(NO)·MnTPP·(MPip) (low-spin, $S = 1/2$) ^[23]	Aver. 2.028(4) Mn ^{II} displaces out of plane to NO by ~ 0.1 Å	2.206(5) MPip 1.644(5) NO	-	-

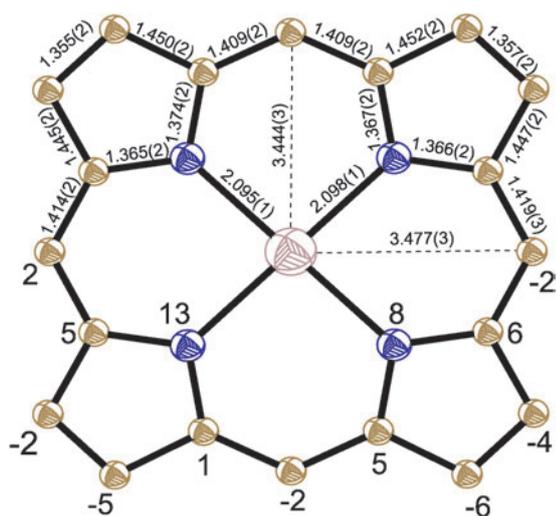


Figure 2. The structure of Mn^{II} TPP porphyrin core in **6**. Upper half shows the structurally independent bond lengths and the lower half shows perpendicular displacements of the atoms (in the 0.01 Å units) from the mean 24-atom porphyrin plane.^[17]

high-spin state of Mn^{II} TPP, which is antibonding relative to the Mn-N(TPP) bonds.

Geometry of Mn^{II} TPP macrocycle is defined to a great extent by the spin state of Mn^{II} atoms. We analyzed the geometric parameters of $(\text{MDABCO}^+)_2 \cdot \text{Mn}^{\text{II}}$ TPP units in the complexes with fullerenes (Figure 2, Table 2). The degree of radial distortion of the porphyrin core can be estimated from the difference in the length of two Mn-C distances, and the perpendicular displacements of the atoms from the 24-atom porphyrin plane (Figure 2). The largest displacements were found for the nitrogen atoms of pyrrole rings (these values are listed in Table 2). The Mn^{II} atoms are positioned exactly in the porphyrin plane in $(\text{MDABCO}^+)_2 \cdot \text{Mn}^{\text{II}}$ TPP when it forms

complex **5**.^[12] That results in the largest radial expansion of the porphyrin core (Table 2). For $(\text{MDABCO}^+)_2 \cdot \text{Mn}^{\text{II}}$ TPP units in **3**, the thermal parameter of Mn^{II} atom for the vibration perpendicular to the porphyrin plane is essentially higher than that of N atoms, and the disorder model in which Mn^{II} atom was distributed between two symmetry equivalent out-of-plane positions with isotropic temperature factors can be applied. However, the accuracy of the crystal structure determination does not allow one to refine simultaneously the position of Mn^{II} atoms with anisotropic temperature factors because they show large correlations.^[12] The out-of-plane displacement of Mn^{II} atoms from the mean porphyrin plane estimated using this model was ± 0.127 Å. In this case moderate radial expansion of the porphyrin core is realized (Table 2). The Mn^{II} atoms arranged exactly in the porphyrin plane in both crystallographically independent $(\text{MDABCO}^+)_2 \cdot \text{Mn}^{\text{II}}$ TPP units in **6** since they are located in the centres of symmetry, whereas the radial expansion of the porphyrin core has moderate values (Table 2). Thus, all $(\text{MDABCO}^+)_2 \cdot \text{Mn}^{\text{II}}$ TPP units manifest radial expansion of the porphyrin core. As this takes place Mn^{II} atoms can locate in the porphyrin plane or displace out of this plane. The transition of Mn^{II} TPP to the low-spin state in $(\text{NO}) \cdot \text{Mn}^{\text{II}}$ TPP·(MPip) decreases in the length of M-N(TPP) bonds (2.028(4) Å), however, the data of the radial expansion of the porphyrin core is absent for this compound.^[23]

Magnetic properties of **3** and **4** are defined by the contribution from $\text{C}_{60}^{\cdot -}$ radical anions and the high-spin Mn^{II} TPP and Fe^{II} TPP porphyrins whereas those of **1** are defined by the contribution from $\text{C}_{60}^{\cdot -}$ radical anions only. The Weiss temperatures were estimated to be -13 K for **1** and -2 K for **2** and **3**. The $(\text{C}_{70}^{\cdot -})_2$ dimers as well as the C_{60}^{2-} dianions are diamagnetic and the magnetic behaviour of **5** and **6** is defined only by the contribution of high-spin Mn^{II} TPP

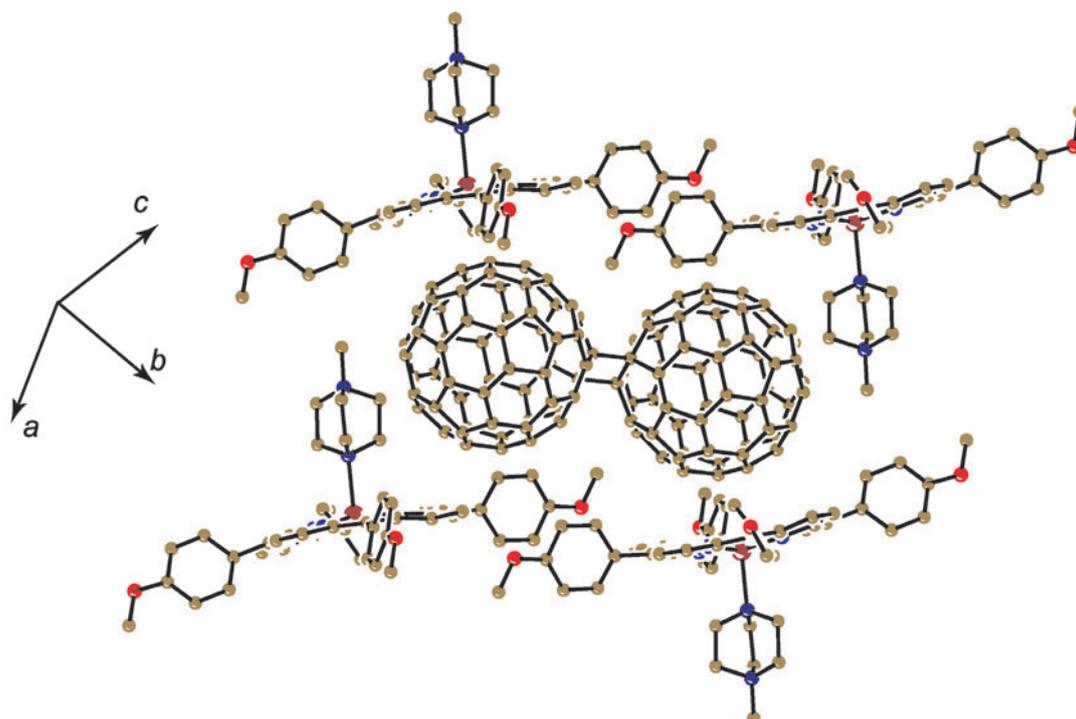


Figure 3. Fragment of the crystal structure of **7** showing the cage from the $(\text{MDABCO}^+) \cdot \text{Co}^{\text{II}}$ TMPP units accommodating the doubly bonded $(\text{C}_{60}^{\cdot -})_2$ dimer.^[13]

molecules which are isolated by the diamagnetic $(C_{70}^-)_2$ dimers or C_{60}^{2-} anions. As a result the Weiss temperatures for these complexes are close to 0.

The formation of $(C_{60}^-)_2$ dimers in the complexes with $(MDABCO^+) \cdot M^{II}TMPP$ units

An ionic complexes **7** and **8** contain negatively charged $(C_{60}^-)_2$ dimers, bonded by two C-C bonds, and the coordination $(MDABCO^+) \cdot M^{II}TMPP$ units ($M = Co$ and Zn). The composition of the complexes was determined by X-ray diffraction on a single crystal (Table 1).

The $MDABCO^+$ cation is a monodentate ligand and coordinates to $Co^{II}TMPP$ in **7** by nitrogen atom with the $Co \cdots N$ distance of 2.385 Å. Cobalt atom is five-coordinated and deviates by 0.084 Å from the plane of four nitrogen atoms towards $MDABCO^+$. Coordination between $Co^{II}TMPP$ and $(C_{60}^-)_2$ dimers is absent, the shortest $Co \cdots C$ distances of 2.757 and 2.940 Å are close to those distances in neutral $Co^{II}TMPP \cdot (C_{60}^-)_2 \cdot (C_6H_5CH_3)_3$ complex (2.65-2.67 Å).^[5] A porphyrin cage accommodates $(C_{60}^-)_2$ dimers in **7** and completely isolates them one from another (Figure 3). Each cage consists of six $\{(MDABCO^+) \cdot Co^{II}TMPP\}$ units, two of which contact with dimer by free $Co^{II}TMPP$ surface, four other units contact with dimer by $MDABCO^+$ cations with short $C(MDABCO^+) \cdots C((C_{60}^-)_2)$ contacts in the 3.082-3.390 Å range (only two of four such units are shown in Figure 3 for clarity).

Similar doubly bonded $(C_{60}^-)_2$ dimers are formed in **8**. However, in this case the shortest $Zn \cdots C((C_{60}^-)_2)$ distances are longer (3.02-3.17 Å). That is due to the stronger coordination of $MDABCO^+$ to $ZnTMPP$ (Figure 4a) since $N(MDABCO^+) \cdots Zn$ distance is noticeably shorter (2.280(4) Å) and the displacement of Zn atom from the plane of four nitrogen atoms towards $MDABCO^+$ is larger (0.265 Å). Short $Co \cdots C((C_{60}^-)_2)$ contacts provide complete order of $(C_{60}^-)_2$ dimers in **7** whereas weaker $Zn \cdots C((C_{60}^-)_2)$ interaction results in the disorder of these dimers in **8** even at 120(2) K in spite of the Van-der-Waals interaction with the porphyrin plane is nearly the same in both complexes. These data allow to suppose that namely metal-fullerene interaction is responsible for the ordering of the fullerene dimers.

The magnetic properties of $(C_{60}^-)_2$ dimers, bonded by two C-C bonds, are of a special interest since they have triplet state at 300 K. Magnetic moment of **7** at this temperature is equal to $3.47 \mu_B$ at 300 K and close to that calculated for a system of four noninteracting 1/2 spins ($\mu_{eff} = 3.46 \mu_B$) per a formula unit. These spins are localized on $Co^{II}TMPP$ and C_{60}^- (four units in total). Taking into account that the dimer is a single molecule, the presence of spins on both C_{60}^- units implies that this dimer should have a biradical state at 300 K. The presence of paramagnetic $Co^{II}TMPP$ and $(C_{60}^-)_2$ is justified by EPR since both species show individual signals. Intense EPR signal with $g = 1.9997$ and the linewidth (ΔH) of 3.46 mT at RT, which is close to those of the radical anions of C_{60} derivatives (2.0000^[24]), was attributed to the $(C_{60}^-)_2$ dimers and broad signal with $g = 2.2638$ and $\Delta H = 30$ mT (19 K) was assigned to $Co^{II}TMPP$. Pure Lorentz shape of the signal from the $(C_{60}^-)_2$ dimers is most probably the result of exchange interaction between $Co^{II}TMPP$ and $(C_{60}^-)_2$, which averages D and E parameters and leads to the disappearance of triplet features of the signal. In contrast to **7** complex **8** contains diamagnetic and EPR silent $(MDABCO^+) \cdot ZnTMPP$ units. That allows us to observe the narrow Lorentz signal from the $(C_{60}^-)_2$ dimers ($g = 2.0024$ and $\Delta H = 0.277$ mT) which narrows at temperature decrease (0.17 mT at 100 K). The data of SQUID measurements for **8** can be fitted according to the Heisenberg model for the pairs of antiferromagnetically interacting spins with exchange interaction between them of $J/k_B = -44.7$ K. Therefore, dimers have singlet ($S = 0$) ground state and excited ($S = 1$) triplet state.

C_{60}^{2-} complexes with $(MDABCO^+) \cdot M^{II}OEP$ units

The complexes **9-12** were obtained by the reduction of C_{60} by CH_3CH_2SNa in the presence of $MDABCO \cdot I$ with following precipitation of the obtained salt in the presence of $M^{II}OEP$. The composition of the complexes **9**, **10** and **12** was determined by X-ray diffraction study on a single crystal whereas that of **11** by elemental analysis (Table 1). The $MDABCO^+$ cations coordinate to $M^{II}OEP$ as monodentate ligands forming positively charged coordination assemblies $(MDABCO^+) \cdot M^{II}OEP$ ($M = Zn, Co, Mn, \text{ and } Fe$). The M^{II} atoms are five-coordinated in these assemblies (Figure 4b).

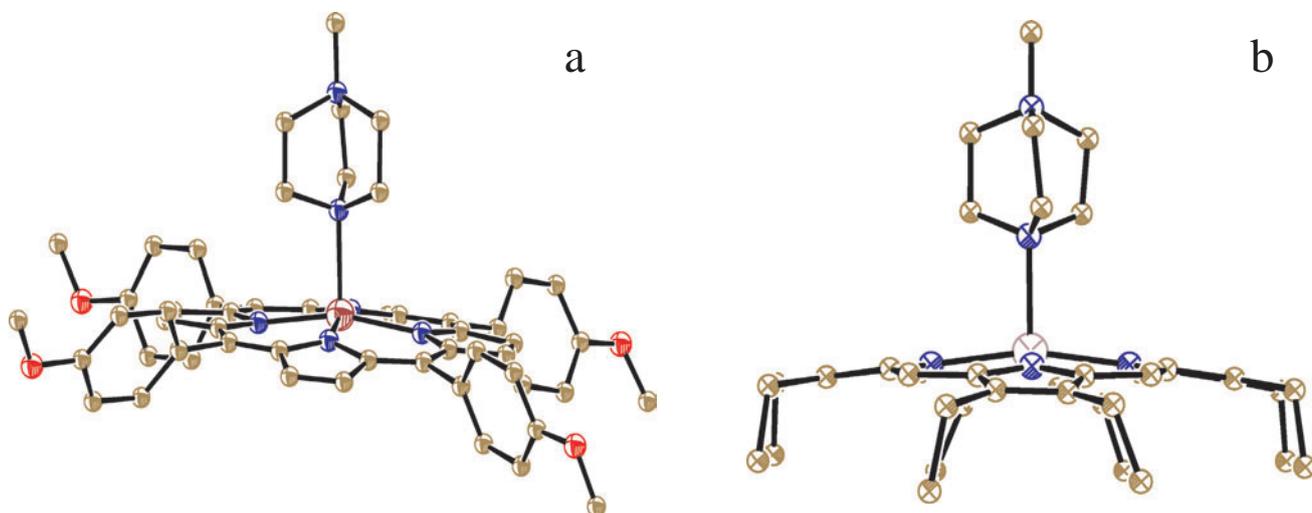


Figure 4. Coordination $(MDABCO^+) \cdot ZnTMPP$ units in **8** (a) and $(MDABCO^+) \cdot Mn^{II}OEP$ units in **12** (b).

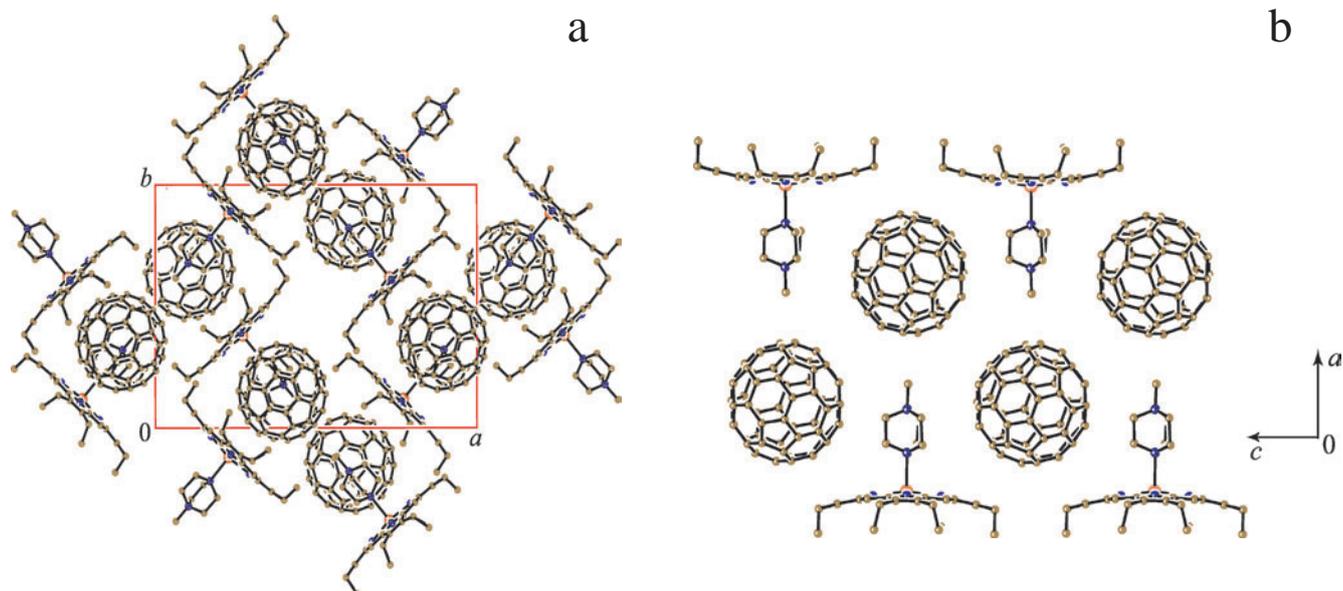


Figure 5. The view on the crystal structure of **9** along *c*-axis and zigzag fullerene chains (a); the view on the zigzag fullerene chains along *b*-axis (b). Solvent molecules are not depicted for clarity.

The length of M-N(MDABCO⁺) bonds changed in the following order: Zn (2.237(2)) < Mn^{II} (2.301(1)) < Co^{II} (2.340(3) Å). M^{II} atoms deviate from the plane of four nitrogen atoms towards MDABCO⁺ cation by 0.042 Å in **10**, 0.239 Å in **9** and 0.274 Å in **12**. The weaker M-N bonds lead to smaller deviation of the metal atom from the plane of four nitrogen atoms. Since one coordination position is free in M^{II} atom C₆₀^{•-} can be a second ligand for M^{II}OEP.

The main structural motif of these complexes is zigzag chains of fullerenes, which occupy channels formed by four M^{II}OEP molecules (Figure 5a). Due to the zigzag arrangement of fullerenes vacancies are formed in the chains, accommodating small MDABCO⁺ cations (Figure 5b). The centre-to-centre distances between fullerenes in the chains are defined by the cation size. They are rather large (10.297 Å for **10**, 10.560 Å for **9** and 10.703 Å for **12**) and do not allow the formation of Van-der-Waals C··C contacts between C₆₀^{•-} in the chains.

C₆₀^{•-} radical anions are arranged from the opposite site of the porphyrin macrocycle relative to the *N*-containing cation. The shortest M··C(C₆₀^{•-}) distance among these complexes was found in **10** (2.508(4) Å at 100 K) and in this case the reversible formation of Co-C coordination bond is observed. M··C(C₆₀^{•-}) distances in **9** and **12** are essentially longer (3.037 and 3.049 Å at 100 K, respectively) indicating the absence of coordination of C₆₀^{•-} to (MDABCO⁺)-ZnOEP or (MDABCO⁺)-Mn^{II}OEP units. Nevertheless, C₆₀^{•-} radical anions form multiple short Van-der-Waals N··C and C··C contacts with the porphyrin macrocycles in these complexes since the macrocycles are concave-shaped and conform well to the spherical shape of C₆₀.

The averaged length of M-N(OEP) bonds in (MDABCO⁺)-Mn^{II}OEP (**12**) is 2.107(2) Å and indicates the high-spin state of Mn^{II}OEP. Close length of Mn-N (porphyrin) bonds was found in high-spin Mn^{II}TPP·(1-MeIm) (2.128(7) Å [26]) and (MDABCO⁺)₂·Mn^{II}TPP (2.081(1)-2.110(2) Å).^[12,17]

Magnetic properties of the complexes range from diamagnetic behaviour of **10** at low temperature (due to the

formation of Co-C(C₆₀^{•-}) bond) to strong antiferromagnetic interaction of spins in **9**, **11** and **12** (the Weiss temperatures were estimated to be -18, -42 and -2.5 K, respectively). Complexes **9** and **12** contain chains of C₆₀^{•-} radical anions, whereas **12** additionally contains high-spin (MDABCO⁺)-Mn^{II}OEP units. Both complexes show AF interaction of spins, which is most probably realized in the fullerene chains. Additionally, each C₆₀^{•-} has face-to-face interaction with the porphyrin macrocycle. Therefore, magnetic interaction between Mn^{II} centres and C₆₀^{•-} is also expected in **12**. The EPR spectrum of **9** justifies the presence of exchange coupling between (MDABCO⁺)-Mn^{II}OEP and C₆₀^{•-}. Complex **11** manifests strongest antiferromagnetic interaction of spins. However, the absence of structural information does not allow the detailed interpretation of the magnetic data for this compound.

Conclusions

The tendency of metalloporphyrins, M^{II} porphyrin, to extra-coordination can be successfully used in the design of supramolecular ionic M^{II} porphyrin-C₆₀ complexes: {(MDABCO⁺)_n·M^{II}porphyrin}·(C₆₀^{•-})·(Solvent)_x (n = 1 and 2). The driving force for the formation of these complexes is the coordination of MDABCO⁺ to M^{II} porphyrin (M = Zn, Co, Mn and Fe). Porphyrins, which cannot coordinate this cation, for example Cu^{II} porphyrins, do not form such complexes.

The synthesis of the series of complexes allows for the first time to study the coordination of MDABCO⁺ and C₆₀^{•-} to M^{II}OEP and compare their coordination ability. There is a competition between fullerenes and *N*-containing cations for the coordination to M^{II}OEP. From structural data we can conclude that fullerenes are weaker ligands than MDABCO⁺. As a result, the M^{II} atoms display out of the porphyrin plane towards *N*-containing ligand forming rather short M-N(L⁺) bonds of 2.237(2)-2.340(3) Å length and that prevents the formation of stable coordination bonds between fullerenes and M^{II} porphyrins. The smaller is the displacement of the

metal(II) atom from the porphyrin plane towards MDABCO⁺ the shorter M··C(C₆₀⁻) contacts are formed. The smallest displacement of Co^{II} atom and the shortest Co··C(C₆₀⁻) distance were found namely in **10**. It should be emphasized that the Co-C coordination bonds are really formed in **10** below 50 K.^[15] In **9** and **12** the larger M··C(C₆₀⁻) distances (> 3 Å) for ZnOEP and Mn^{II}OEP indicate the absence of coordination at 100 K.

Coordination assemblies were found in a series of {(MDABCO⁺)₂·M^{II}TPP}·(C₆₀⁻)₂·(Solvent)_x complexes with metal(II) tetraphenylporphyrins (M=Zn, Co, Mn and Fe).^[12] However, in this case two MDABCO⁺ cations coordinate to each M^{II}TPP with the formation of (MDABCO⁺)₂·M^{II}TPP units and, as a result, the central metal(II) atoms of porphyrins are shielded from bonding with C₆₀⁻. In the case of six-coordinated metalloporphyrins M-N(L⁺) bonds are rather long (2.475(2)-2.553(2) Å) indicating essential destabilization of these coordination units. The Mn^{II} and Fe^{II} porphyrins are in high-spin state (S = 5/2) and (S = 2), respectively both for five- and six-coordinated porphyrins in the complexes with fullerenes. That was confirmed by the magnetic measurements.

The developed method of synthesis demonstrates high potential for the preparation of different σ-bonded structures of negatively charged fullerenes and coordinatively bound structures of metalloporphyrins with N-containing cations as well to obtain complexes with antiferromagnetic interaction of spins ranging from weak to strong.

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