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Synthesis and characterisation of C_{60} and C_{70} molecular complexes with metal tetraphenylporphyrins MTPP, where M=Mn, Co, Cu, Zn.

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Abstract

New molecular complexes of fullerenes C_{60} and C_{70} with metal tetraphenylporphyrins, MTPP, where M = Mn^{II}, Co^{II}, Cu^{II}, and Zn^{II}, have been synthesised. Crystal structures of C_{60} and C_{70} complexes with CuTPP and ZnTPP*Py have been discussed. The fullerene molecules form zigzag chains in $CuTPP{\cdot}C_{70}(C_7H_8)_{1.5}(C_2HCl_3)_{0.5}$, columns in $(CuTPP)_2C_{60}$ and are isolated from one another in the fullerene complexes with ZnTPP*Py. Copper in $(CuTPP)_2C_{60}$ and zink in the fullerene complexes with ZnTPP*Py form no shortened contacts with fullerenes whereas the CuTPP molecules are weakly coordinated with C_{70} in $CuTPP{\cdot}C_{70}(C_7H_8)_{1.5}(C_2HCl_3)_{0.5}$. Complex formation with fullerenes affects the ESR spectra of MTPP (M = Mn, Co and Cu). MnTPP in the complex with C_{70} lowers its spin state from S=5/2 to S=1/2, whereas CoTPP and CuTPP change the constants of hyperfine interaction.

Keywords: fullerenes C_{60} and C_{70}, metal tetraphenylporphyrins, molecular complexes, X-ray crystal structure, ESR-spectroscopy.

Up to now a great number of fullerene complexes with different organic donors has been synthesised [1.2]. The complexes with porphyrins are of a special interest as promising photoactive materials [3]. It is known that $Mn^{II}TPP$ forms ferromagnetic ion-radical salts with tetracyanoethylene [4]. Acceptor fullerenes molecules can also be used in the design of molecular magnetic compounds.

The formation of a variety of compounds ranging from molecular complexes to ion radical salts is possible between fullerenes and porphyrins. $Cr^{II}TPP$ and $Sn^{II}TpTP$ reduce C_{60} to form ion radical salts [5,6]. Octaethylporphyrin and octakis(dimethylamino)porphyrazine metal derivatives and some substituted porphyrins form molecular complexes with fullerenes [7-9].

In this work we report the synthesis and characterization of new molecular complexes of fullerenes C_{60} and C_{70} with Mn^{II}, Co^{II}, Cu^{II}, and Zn^{II} tetraphenylporphyrins.

The novel molecular complexes $MnTPP{\cdot}C_{70}(CS_2)_{1.25}$ (**1**); $CoTPP{\cdot}C_{60}(CS_2)_{0.5}$ (**2**); $CoTPP{\cdot}C_{70}$ (**3**); $(CuTPP)_2C_{60}$ (**4**); $CuTPP{\cdot}C_{70}(C_7H_8)_{1.5}(C_2HCl_3)_{0.5}$ (**5**); $(ZnTPP{\cdot}Py)_2C_{60}$ (**6**); $(ZnTPP{\cdot}Py)_2C_{60}{\cdot}Cp_2Fe{\cdot}C_7H_8$ (**7**); $(ZnTPP{\cdot}Py)_2C_{70}{\cdot}C_7H_8{\cdot}(C_2HCl_3)_x$ ($x\approx0.5$) (**8**) were obtained by evaporating solutions containing fullerene and the corresponding porphyrin in CS_2 (**1-3**), toluene (**4, 5**), and trichloroethylene/pyridine (**6-8**). Ferrocene was added to crystallize **4** and **7**, however, it is involved only in the crystal structure of **7**.

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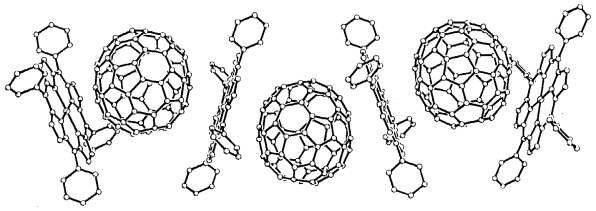

Fig.1. Chains of alternating C_{70} and CuTPP molecules in **5** [10].

Crystal structures.

The structure of **4** [10] contains no solvent molecules. Fullerene molecules are arranged in slightly non-linear columns, whereby each fullerene molecule contacts two others with the centre-to-centre distance of 9.92 Å and the shortest C···C distances of 3.1-3.4 Å. The columns are separated from one another by pairs of twisted CuTPP molecules. The shortest intermolecular distances N···C(C_{60}) of 3.36 Å and Cu···C(porphyrin) of 3.28 Å are characteristic of van der Waals interactions, and there are no shortened Cu···C(C_{60}) contacts.

The C_{70} molecules are fully ordered in **5** [10]. Ellipsoidal C_{70} molecules form zigzag chains in which each C_{70} molecule has two adjacent C_{70} molecules, with close van der Waals contacts (C···C 3.2-3.4 Å) and centre-to-centre distances of 10.14 and 11.13 Å. Each C_{70} is sandwiched between two CuTPP molecules (Fig. 1) with the Cu···C(C_{70}) distances varying from 2.88 to 3.03 Å. These distances can be described as a secondary bonding, which was reported earlier for some fullerene complexes [7-8].

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Fullerene molecules are isolated from one another in isomorphous complexes (**7**) and (**8**) and are sandwiched between two porphine molecules. Zinc atom in the ZnTPP*Py molecule is protruded towards the pyridine ligand with short Zn···N(Py) distances of 2.12-2.15 Å. All intermolecular contacts in the complexes have typical van der Waals lengths with the Zn···C(fullerene) distances of 3.08-3.32 Å and the shortest N(ZnTPP)···C(fullerene) distance of 3.1 Å. The major difference between **7** and **8** is the presence of ferrocene molecule in the former case. Ferrocene molecules have no direct contacts with C_{60} in the complex **7**. Probably ferrocene molecule can be substituted by other molecules of similar size.

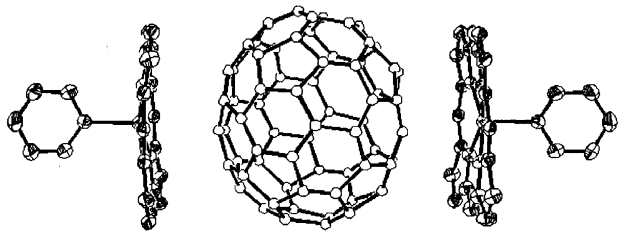

Fig.2. Co-orientation of C_{70} and ZnTPP*Py molecules in **8**. Phenyl groups of ZnTPP are omitted

ESR spectra.

The ESR spectra of MnTPP, CoTPP and CuTPP and their complexes with C_{70} at 77 K are shown in Fig. 3 [10, 11].

The spectra of the C_{60} complexes with the same donors are similar. Pure MnTPP has a high spin state (S=5/2) and an anisotropic ESR spectrum ($g\perp$ = 5.9, $g\parallel$ =2.0) with a hyperfine structure (HFS) [11]. The spectrum of **4** (Fig. 3 b) is a broad line with g = 2.002 and ΔH_{pp} = 300G and corresponds to low spin state (S=1/2) of MnTPP. A similar spin lowering occurs upon the formation of the nitric oxide complexes $Mn^{II}TPP(X^-)(NO^+)$ (X = Cl, CH_3CO_2) [12]. The exposure of **4** to air for a few hours results in the disappearance of the ESR signal due to oxidation of the Mn^{II} to diamagnetic Mn^{III}.

In complexes **2-5** the CoTPP and CuTPP have a low spin state (S=1/2) and ESR spectra with the resolved HFS and *g*-factor anisotropy. The effect of complexation is almost confined to the hyperfine interaction (HFI) parameters, which are the most sensitive to local interactions on the metal centres. Due to short relaxation times, ESR of pure CoTPP is observed only at 77 K (Fig. 3c), while the spectra of **2** and **3** (Fig. 3 d) are observed even at room temperature. Both complexes display a broad intense asymmetric line with <g>=2.4 and ΔH_{pp} = 500-600G, resulting from the overlap of parallel and perpendicular components of the spectrum. HFS stipulated by the interaction of an unpaired electron with the ^{59}Co nucleus (I=7/2) is also observed above a broad signal, as eight components with a separation of 170 G. The *g*-factors change substantially relative to pure CoTPP, both HFI constants A and B decrease, suggesting weak CoTPP...fullerene interactions, probably similar for C_{60} and C_{70}.

The ESR spectra of CuTPP in the complexes **4-5** preserve the $g\perp$ and $g\parallel$ values. However, the intensity of the perpendicular component increases in **5** (Fig. 3f). This indicates a less anisotropic interaction of the spin orbitals, probably due to weak Cu...C_{70} coordination, such as we observed in the crystal structure of **5**.

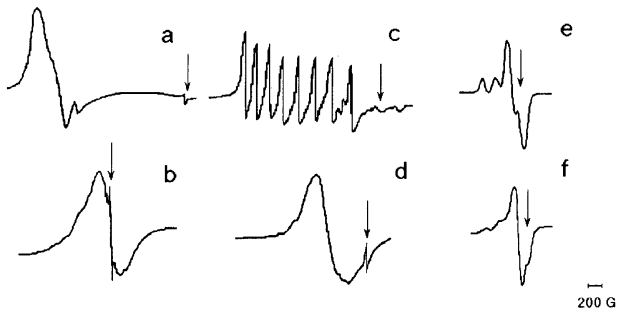

Fig.3. The ESR spectra of (a) MnTPP; (b) **1**; (c) CoTPP; (d) **3**; (e) CuTPP; and (f) **5** at 77 K in argon atmosphere. Arrows show the position of g=2.0022.

All the complexes are dielectrics with conductivity $<10^{-7}$ $S \cdot cm^{-1}$. According to ESR, conductivity and crystallographic data, **1-8** are molecular complexes. The absence of charge transfer from MnTPP to C_{70} in **1** and a low-spin state of MnTPP therein, do not allow a molecular ferromagnet to be obtained. The interaction between the components in all the compounds is mainly of van der Waals nature, with a probable contribution of $C_{60(70)}$···N(MTPP) π-π interactions and the secondary π-d MTPP···$C_{60(70)}$ bonding, the latter slightly affects the electronic state of MTPP. According to the ESR spectra of MTPP the effect of complexation with fullerenes decreases in the succession MnTPP>CoTPP>CuTPP. Although the Cu···C_{70} interactions in **5** are rather weak, they compare favourably with the absence of such interactions in **4**. Probably this effect may be utilised to separate chromatographically C_{60} from C_{70}, using appended MTPP.

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