The design of ionic complexes of fullerenes manifesting magnetic transitions and high conductivity

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The design of multicomponent ionic complexes of fullerenes, $(D_1^+)\cdot(C_{60}^-)\cdot(D_2)$ is discussed. In this approach D_1 was an organic cation and D_2 was a neutral structure-forming molecule. These complexes demonstrated paramagnetic-diamagnetic transitions associated with the C-C and M-C bond formation, singlet-triplet transitions and high conductivity.

1. $(D^+)\cdot(C_{60}^-)\cdot Co^{II}OEP$ contain tetramethylphosphonium (**1)** and *N*-methyldiazabicyclooctane ($MDABCO^+$ **(2))** cations. Diamagnetic σ-bonded $\{Co^{II}OEP\cdot(C_{60}^-)\}$ anions in **1** do not dissociate up to 290K. In **2** both $MDABCO^+$ and C_{60}^- coordinate to $Co^{II}OEP$ and reversible dissociation of the Co-C(C_{60}^-) σ-bond is observed at 50-250K. The dissociation is accompanied by transition from diamagnetic to paramagnetic state [1].

2. Unusual $(C_{60}^-)_2$ dimer bound by two C-C bonds was found in $\{(MDABCO^+)\cdot Co^{II}TMPP\}_2\cdot(C_{60}^-)_2$. The dimer has a biradical state (S = 1) at 300 K. The EPR behaviour of the dimer was described within the model for triplet excited (S = 1) and singlet ground states (S = 0) with the energy gap of 70 ± 2 cm^{-1} [2].

3. Complexes of C_{60}^- and C_{70}^- anions with coordination $(MDABCO^+)_2\cdot M^{II}TPP$ assemblies (M = Zn, Co, Mn, Fe) involve layers formed by $(MDABCO^+)_2\cdot M^{II}TPP$ and zigzag chains of $C_{60}^{\bullet-}$. In the zigzag chains $C_{60}^{\bullet-}$ spins are antiferromagnetically coupled. The C_{70} complexes contain diamagnetic $(C_{70}^-)_2$ dimers linked by one C-C bond [3].

4. The $(D^+)\cdot(C_{60}^{\bullet-})\cdot$TPC complex manifests metallic behaviour. In the complex there are two types of closely packed hexagonal layers built of monomeric C_{60}^- anions. Different environment of C_{60}^- anions provides different rotation freedom. The effect of the rotation of C_{60}^- anions on metallic conductivity is discussed.

5. Complexes $(D^+)_2\cdot(C_{60}^{\bullet-})_2\cdot$ET contain double chains formed by $C_{60}^{\bullet-}$ and manifest reversible dimerization of $C_{60}^{\bullet-}$ in the 250-280K range. The crystal structures of monomeric and dimeric phases and the changes of the magnetic properties of the complexes at the dimerization are discussed.

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[3] D.V. Konarev, S.S. Khasanov, A. Otsuka, et.al., *Inorg. Chem.* (2007), in press.