

Ionic complexes containing fullerene anions and negatively charged phthalocyanine structures

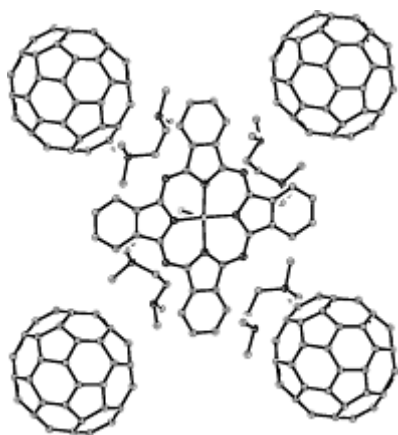
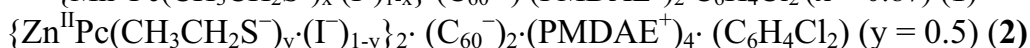
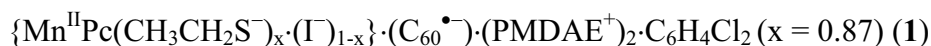
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At present great attention is given to the synthesis and study of ionic complexes of fullerenes with metalloporphyrines. This is due to interesting magnetic properties [1] and a possibility to investigate different negatively charged σ -bonded structures of fullerene in such complexes [2]. Phthalocyanines represent another large class of macrocycles. However, ionic fullerene complexes with phthalocyanines have not been obtained so far. Here we present the first ionic complexes containing simultaneously fullerenes anions and negatively charged coordination phthalocyanine structures:



Both compounds have been obtained as single crystals that allowed their crystal structure to be studied. In complex **1** fullerene radical anions form honeycomb-like loose layers in which each fullerene has three neighbors with centre-to-centre distances of 10.130–10.289 Å. The absence of Van der Waals contacts between fullerenes results in that $\text{C}_{60}^{\bullet-}$ remains monomeric in this complex at 110(2) K. In complex **2** fullerenes form dimers $(\text{C}_{60}^-)_2$ bonded by one C-C bond. Dimers are packed in corrugated honeycomb-like layers with distances between fullerene centres equal to 9.898–10.107 Å. At the coordination of iodine or ethanethiolate

anions on the central metal atom, phthalocyanines of Mn(II) and Zn(II) form unusual negatively charged coordination structures $\text{M}^{\text{II}}\text{Pc}(\text{anion}^-)$, which are packed in the $\{\text{M}^{\text{II}}\text{Pc}(\text{anion}^-)\}_2$ dimers with short interplanar distance of 3.142 Å in **1** and 3.274 Å in **2**. Phthalocyanine dimers also form layers with the PMDAE^+ cations and these layers alternate with the fullerene ones. The packing of spherical fullerenes with planar phthalocyanines in a crystal is attained by the introduction of fullerenes between two phenylene groups of phthalocyanine. The π - π interaction between porphyrin macrocycle and fullerene hexagonal or pentagonal rings characteristic of previously studied ionic porphyrin-fullerene complexes is not realized in complexes **1** and **2**.

- [1] D.V. Konarev, S.S. Khasanov, G.R. Mukhamadieva, L.V. Zorina, A. Otsuka, H. Yamochi, R.N. Lyubovskaya, *Inorg. Chem.* **49**, 3881 (2010).
 [2] D.V. Konarev, S.S. Khasanov, A. Otsuka, G. Saito, R.N. Lyubovskaya. *J. Am. Chem. Soc.* **128**, 9292 (2006).