# Thianthrene Radical Cation Hexafluorophosphate

Johannes Beck[a], Thomas Bredow[b], and Rachmat Triandi Tjahjanto[a]

[a] Institute of Inorganic Chemistry, Bonn University, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany
[b] Institute for Physical and Theoretical Chemistry, Bonn University, Wegelerstr. 12, 53115 Bonn, Germany

Reprint requests to Prof. Dr. J. Beck. Fax: +49 (228) 73 5660. E-mail: j.beck@uni-bonn.de

*Z. Naturforsch.* **2009**, *64b,* 145 – 152; received September 16, 2008

In the presence of $[NBu_4][PF_6]$ as the electrolyte, thianthrene (TA) is transformed by electrochemical oxidation to thianthrenium hexafluorophosphate containing the $TA^{\bullet+}$ radical cation. The reactions were performed in $CH_2Cl_2$, $H_3CCN$, and liquid $SO_2$ as solvents. In $CH_2Cl_2$, $TA[PF_6]$ is sparingly soluble and is deposited directly in crystalline form on the platinum electrode. In $H_3CCN$ and liquid $SO_2$, $TA[PF_6]$ is highly soluble and gives dark blue solutions from which it can be crystallized upon concentration of the solutions. The air sensitive crystals are black with bronze metallic luster. They belong to the monoclinic system (*C*2/*m*, $a$ = 12.4345(8), $b$ = 10.5318(6), $c$ = 11.1303(7) Å, $\beta$ = 112.565(3)°) and are built up of almost planar $TA^{\bullet+}$ cations and octahedral $[PF_6]^-$ anions. The F atoms of the anions are disordered over two positions. The radical cations are associated to form dimeric units $(TA^{\bullet+})_2$ with the planar molecules stacked with two weak S···S bonds (3.06 Å). In the crystal these dimers are separated by the $[PF_6]^-$ anions. Electrical conductivity measurements show $TA[PF_6]$ to be a small-gap semiconductor. Conductivity is low at r. t. but reaches $2.5 \cdot 10^{-5}$ S m$^{-1}$ at 110 °C, the activation energy in the high-temperature region amounts to 1.2 eV. Periodic quantum-chemical calculations at hybrid density-functional level predict a strong coupling between neighboring ($TA^{\bullet+}$) spin centers, resulting in a singlet ground state. The calculated band gaps of both singlet (1.5 eV) and triplet (0.9 eV) states are small, consistent with the measured conductivity.

*Key words:* Thianthrene, Radical, Hexafluorophosphate, Conductivity, Band Structure, Crystal Structure