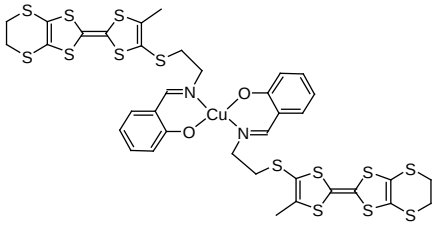
Synthesis of New TTF-Based Metal Complexes for Conducting and Magnetic Systems: Schiff Base-Type Metal Complex with Partially Oxidized TTF Moiety

Hiroyuki Nishikawa, Hironori Oshima, Kazuyo Narita, and Hiroki Oshio
Graduate School of Pure and Applied Sciences, University of Tsukuba, Japan
Email: nishikaw@chem.tsukuba.ac.jp

Interaction between conduction electrons and localized spins has lead to attractive physical properties both for inorganic solids and organic molecular based materials. The molecular based materials exhibiting multifunctional properties originating such interaction, like paramagnetic superconductor or magnetic field induced superconductivity, are referred as π-d systems. In the π-d systems, interaction between conduction electrons and localized spins is usually weak, because they have been constructed with two component molecules: tetrathiafulvalene (TTF) derivatives and counter anions with paramagnetic metal ions. In order to develop molecular based materials with stronger interaction between conduction electrons and localized spins, a number of researches for the synthesis of TTF derivatives possessing a direct coordination site to paramagnetic metal ions have been conducted. In the metal complexes involving TTF units in the ligands reported so far, the TTF moieties were neutral or completely oxidized to a cation radical $TTF^{+\cdot}$, leading to the low electrical conductivity. As most of the ligands in such complexes were monodentate, the complexes might not be stable against oxidation of the TTF moieties.

We have prepared several TTF derivatives involving Schiff base type ligands which can coordinate to metal ions by chelate structure. Among them, HsaeTTF (4-(2-salicylideneiminoethylthio)-5-methyl-4',5'-ethylenedithio-TTF) yielded metal complexes with Ni(II) and Cu(II) ions, $[M^{II}(saeTTF)_2]$ (M = Ni^{2+} and Cu^{2+}), which were stable upon electrochemical oxidation of TTF moieties due to the stable complexation. We successfully obtained a Cu(II) complex with a partially oxidized TTF, $[Cu^{II}(saeTTF)_2]PF_6$, crystal structure of which is consist of 1-D column of partially oxidized TTF units. We will report the synthesis, crystal structure and physical properties including electrical conductivity and magnetism of this salt.



$[Cu(sae\text{-}TTF)_2]$