

Title

Preparation and physical properties of molecular conductors based on novel tto (tetrathiooxalate)-bridged polymetallic dithiolene complexes

Abstract

New polymetallic Ni and Pd complexes bridged by tto (tetrathiooxalate) ligands have been synthesized by a new direct reaction of the tto ligand with a mono-nuclear metal complex in order to construct new molecular conductors. Synthesis of this type of polymetallic complexes with dmit or dimse ligands was reported by other groups. Their reactions are based on mixing of the tto ligand with the dithiolene ligand and the metal ion. According to their method, we have obtained a di-nuclear Pd complex containing the dmit ligands, $(\text{Bu}_4\text{N})_2[(\text{tto})\text{Pd}_2(\text{dmit})_2]$ with a reaction of tto^{2-} , Cs_2dmit , Bu_4NBr and K_2PdCl_4 in MeOH/acetone at r. t. under Ar. However, this method was not suitable for the synthesis of polymetallic Ni complexes with other dithiolene ligands. We have found that various polymetallic Ni complexes, $[(\text{tto})\text{Ni}_2(\text{S-S})_2]^{m-}$ and $[(\text{tto})_2\text{Ni}_3(\text{S-S})]^{m-}$; S-S = edo, dddt, tdas; $m = 1, 2$) can be formed from the new reaction of tto^{2-} with mono-nuclear $[\text{Ni}(\text{S-S})_2]^{n-}$ ($n = 0, 1$) metal complexes in acetonitrile (r. t.) or DMF (80 °C) under Ar. Obtained complexes were purified by HPLC equipped with a ODP column using acetonitrile/ H_2O (95:5). Single crystals of these polymetallic complexes were obtained by recrystallization from acetone/2-propanol or acetonitrile. Crystal structure analyses and resistivity measurements for the single crystals were performed. Details of synthesis and physical properties will be discussed.