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Substituting Se for S in Gold Bisdithiolene Thiophenic Complexes

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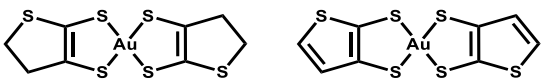
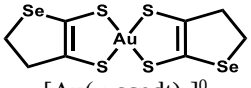
Single Component Molecular Metals (SCMM) are solids based on neutral molecules that display properties characteristic of metals, which are believed to rise from the intermolecular interactions in the solid state.[1,2] The gold bisdithiolene complex $[Au(\alpha\text{-tpdt})_2]^0$, is one of the first known examples of the SCMM. This small neutral molecule displays, as a polycrystalline sample, a room temperature conductivity, σ_{300K}, of 6 Scm^{-1}. The gold bisdithiolene complex $[Au(\alpha\text{-dtpdt})_2]^0$, with a very similar structure but with a tetrahydrothiophene instead of a thiophene ring, displays a much smaller room temperature conductivity, σ_{300K} = ~7x10^{-3} Scm^{-1}, also as a polycrystalline sample.[3]
As part of a study of the selenium analogues of these compounds, and in order to understand the role of the peripheral thiophene ring in the transport properties of these solids, we report here new gold bisdithiolene complexes with selenium instead of sulfur in the thiophene/tetrahydrothiophene moieties. Two new gold bisdithiolene complexes, $[Au(\alpha\text{-spdt})_2]$ and $[Au(\alpha\text{-scpdt})_2]$, were prepared and characterised both in monoanionic and neutral state. These neutral complexes were obtained by oxidation of the correspondent tetrabutylammonium salts which, in turn, were obtained from the synthetized selenolo[2,3-*d*]-1,3-dithiole-2-thione and 5,6-dihydroselenolo[2,3-*d*]-1,3-dithiole-2-thione compounds, respectively.[4]
The electrical transport properties of $[Au(\alpha\text{-spdt})_2]^0$ were measured in a polycrystalline sample revealing a semiconducting behavior with σ_{300K} = 7.2x10^{-3} $S.cm^{-1}$ and an activation energy, Ea, of 195 meV. The magnetic susceptibility revealed a behaviour reminiscent of Pauli paramagnet, with a room temperature paramagnetic susceptibility, χ_p, of 1.03x10^{-4} emu/mol, while $[Au(\alpha\text{-scpdt})_2]^0$ measured in a single crystal, displayed σ_{300K} = ~0.1 $S.cm^{-1}$ with a smaller Ea of 95 meV.
$[Au(\alpha\text{-spdt})_2]^0$ and $[Au(\alpha\text{-scpdt})_2]^0$ are the first complexes of a new family of transition metal bisdithiolene and bisdiselenolene with selenophene/selenacyclopentane rings, that we intend to study.

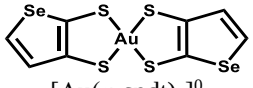


$[Au(\alpha\text{-dtpdt})_2]^0$

$[Au(\alpha\text{-tpdt})_2]^0$



$[Au(\alpha\text{-scpdt})_2]^0$



$[Au(\alpha\text{-spdt})_2]^0$

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