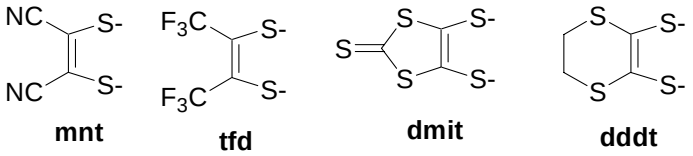
Crystalline Paramagnetic Dithiolene Complexes: From Square-Planar Complexes with Secondary Coordination to Heteroleptic Cyclopentadienyl/Dithiolene Complexes : Spin Chains and Ladders, Antiferromagnets

Marc Fourmigué

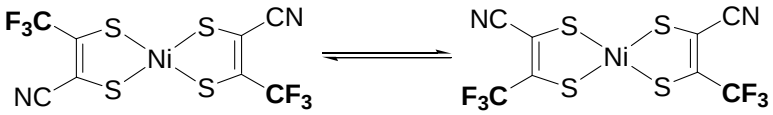
Sciences Chimiques de Rennes, Univ. Rennes 1 & CNRS, Campus de Beaulieu, 35042 Rennes, France.
Email marc.fourmigue@univ-rennes1.fr; http://www.scienceschimiques.univ-rennes1.fr/macse

Due to the non-innocent character of the dithiolene ligand, metal dithiolene complexes have been investigated since the early sixties for the numerous oxidation states a given complexes is able to sustain. The variety of stable open-shell complexes available, such as those derived from the mnt, tfd, dmit or dddt ligands, has allowed the isolation of numerous magnetic, conducting or super-conducting materials.



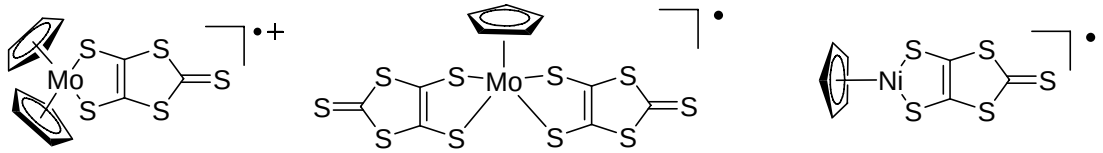
We will describe our own results on:

1) the secondary coordination of dithiolene complexes bearing extra coordination sites. A novel 1,2−dithiolate ligand [1], substituted with both CN and CF_3 groups (tfadt), is described together various salts of the S=1/2 complexes $[Ni(tfadt)_2]^{-\bullet}$ and $[Cu(tfadt)_2]^{2-}$ with TTF, BEDT-TTF, perylene [2], and ferrocene [3]. They exhibit rich structural and magnetic properties, characterized by concomitant order-disorder and magnetic first-order transitions. Besides, coordination chains with alternating S=½, S=1 or S=½, S=5/2 systems have been obtained with $Mn(TPP)^{+}$ or $Ni(cyclam)^{2+}$, characterized by antiferro-magnetic and ferro-magnetic coupling respectively.



trans-$[Ni(tfadt)_2]$ *cis*-$[Ni(tfadt)_2]$

2) non-planar radical complexes such as those derived from mixed-ligand complexes associating cyclopentadienyl and dithiolene complexes. These complexes, either in their d^1 form as $[Cp_2Mo(dmit)]^{+\bullet}$ [4] or in their d^7 form as in $[CpNi(dmit)]^{\bullet}$ [5], adopt several solid state organisations, and accordingly several magnetic ground states, depending upon the extend of delocalisation of the spin density between the metal and dithiolene moieties.



[1] O. Jeannin, J. Delaunay, F Barrière, M. Fourmigué, *Inorg. Chem*. **2005**, *44*, 9763.
[2] O. Jeannin, M. Fourmigué, *New J. Chem*. **2006**, *30*, 1774
[3] O. Jeannin, R. Clérac, M. Fourmigué, *J. Am. Chem. Soc.* **2006**, *108*, 14649
[4] M. Fourmigué, *Acc. Chem. Res*. **2004**, *37*, 179
[5] (a) M. Fourmigué, N. Avarvari, *Dalton Trans.* **2005**, 1365 ;
(b) M. Nomura, T. Cauchy, M. Geoffroy, P. Adkine, M. Fourmigué, *Inorg. Chem*. **2006**, *45*, 8194
(c) M. Nomura, M. Geoffroy, P. Adkine, M. Fourmigué, *Eur. J. Inorg. Chem.* **2006**, 5012