

**Strongly Correlated Systems: a Density Functional Theory Approach to the Study of
Valence Tautomeric Interconversion in a Cobalt Open Shell Complex**

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Valence tautomerism is a very interesting property exhibited by molecular systems constituted by a metal complexed with redox-active ligands. This phenomenon is the interconversion between two tautomeric forms of the complex, each having a different total spin number S . A very important fact from the practical point of view is that an equilibrium between the two states is achieved which is governed, and hence may also be regulated, by relatively small changes in temperature, pressure and optical irradiation. Compounds belonging to the class of ionic compounds of formula Co(L)(diox)Y (L = tetraazomacrocyclic ligand, Y = mononegative anion) constitute a good example: they behave as electronic switches at molecular level, showing temperature and pressure induced intramolecular one electron transfer equilibrium. Self-consistent field (SCF) single point and geometry optimization calculations have been performed with different density functional theory based programs. The results are presented for the various spin states and tautomeric forms of *o*-dioxolene adduct[#] of the $\{\text{Co(CTH)(Phendiox)}\}^+$ complex (CTH=dl-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetra-decane; phendiox= 9,10-dioxophenantrene). In addition to these, *ab initio* MCSCF calculations are running in order to get better insight in the electronic structure of the two tautomers.

[#]A. Caneschi, A. Dei, F. Fabrizi de Biani, P. Gülich, V. Ksenofontov, G. Levchenko, A. Hofer, F. Renz, *Chemistry Eur. J.*, (2001), 7, 3926; A. Caneschi, A. Dei, D. Gatteschi, V. Tangoulis, *Inorg. Chem.* (2002), *accepted for publication*