

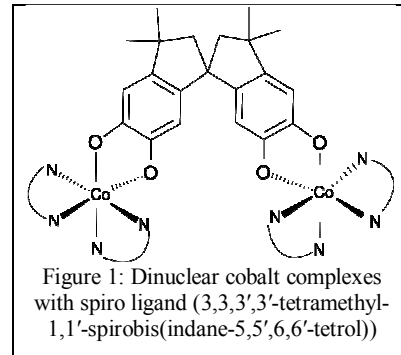
# Binuclear cobalt Coordination Compounds of Spiro-dioxolene

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Bistable compounds are known by the presence of quasi-degenerated states which are accessible by external stimulus such as heat, pressure and light.<sup>1</sup> In the valence tautomers, a kind of bistable compound, the bistability is due to the existence of electron transfer between redox active ligands and metal, combined with a change in the electronic multiplicity of the metallic center. These changes induce variations in the optic and magnetic properties of these materials. Among the many different systems presenting valence tautomeric characteristics, most of the examples are formed by cobalt and dioxolenes.<sup>1</sup> In these compounds ligand-metal electron transfer occurs to the changes in metal electronic multiplicity, creating the equilibrium  $LS-[Co^{3+}(cat)(sq)] \leftrightarrow HS-[Co^{2+}(sq)_2]$ , in which *cat* stands cathecolate dianion and *sq* semiquinonate. Dinuclear complexes showing two step transitions are of particular interest since these transitions can be used to form a three-state molecular device. Two-step transition valence tautomers can be synthesized using a bis-bidentated dioxolene ligand derived of a spiro ring.<sup>2</sup> Additionally, the influence of redox innocent ancillary ligands in the interconversion of valence tautomers is well established, in particular regarding the stabilization of the equilibrium between HS-Co(II) and LS-Co(III). Aiming to study this influence, a series of amine ligand were used as ancillary ligand in the synthesis of cobalt and spiro complexes. The ancillary ligand chosen in this studies are 2,2'-bipyridine, ethylenediamine, pyridine and 2-(1H-imidazol-2-yl)pyridine. Preliminary spectroscopy characterization indicated the formation of complexes by the decrease of intensity in the strong bands associated with cathecolate form in dioxolenes. Those characteristic bands 1254, 1290, 1360 and 1440  $cm^{-1}$  have changed their frequencies or even disappeared, evidencing the formation of coordination compounds.<sup>2,3</sup> Electronic absorption spectra in UV-vis region are characterized by the formation of broad bands in the region 700-500 nm that assigned LMCT bands.<sup>2</sup> The intense band centered in 390 nm ( $\pi \rightarrow \pi^*$ ) in the free spiro ligand shifted to lower energies, while broad shoulders appear in the spectra of all complexes, making it hard the assignment of the cobalt oxidation state. Indeed, this can suggest the presence of tautomeric equilibrium. Further spectroscopy investigation using EPR and XAS are being carried out in different temperatures to determine the equilibrium between the tautomeric species. *Ab initio* calculation will be used to study the electronic structure and support the assignment of vibrational and absorption spectra of all complexes. Moreover, crystallization assays are in progress to obtain single crystals to structural determination by X-ray diffraction.



<sup>1</sup>Shultz, D. A. Valence tautomerism in dioxolene complexes of cobalt. In: *Magnetism: Molecules to Materials II*. [S.l.]: Wiley-VCH Verlag GmbH & Co. KGaA, 2003, cap. 8, p. 281-306.

<sup>2</sup>Alley, K. G., et. al. *J. Am. Chem. Soc.* 2013, 135, 8304–8323.

<sup>3</sup>Patricia, T. T., et al. *Phys. Chem. Chem. Phys.*, 2012, 14, 1038–1047.