

Thermal- and pressure-induced transformation of new valence tautomeric complex

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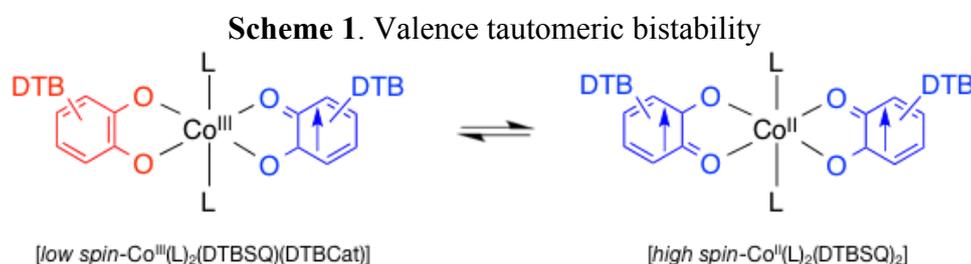
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Molecule-based systems that respond to external stimulus such as heat, light, and magnetic and electric fields have attracted considerable attention because they have great scientific and technological potential as molecule-based devices, i.e., low-energy driven switches, memories, information storages, and sensors in environment.¹

Valence tautomerism (VT) is the property to show reversible change between two or more tautomers differing in their charge distribution. In particular, a family of cobalt-dioxolene complexes of *low spin*-[Co^{III}(L)₂(DTBSQ)(DTBCat)] undergoes reversible VT shifts to *high spin*-[Co^{II}(L)₂(DTBSQ)₂], where DTBSQ⁻ and DTBCat²⁻ refer to a monoanionic di-*tert*-butylsemiquinonato and a dianionic di-*tert*-butylcatecholato forms, respectively, and L is a nitrogen-containing auxiliary ligand (Scheme 1). The most prominent feature of VT interconversion is that the two tautomers are related by an intramolecular single-electron transfer between DTBCat and the Co^{III} ion as well as a spin change from a *low-spin* Co^{III} form ($S = 1/2$) to a *high-spin* Co^{II} form ($S = 3/2$ with two $S = 1/2$). VT complexes show VT behavior induced by heat, high pressure, and photoirradiation at low temperature.²

In this work, we present thermal- and pressure-induced VT behavior of newly synthesized cobalt complexes. The detailed VT behavior, together with changes of the electronic states, will be presented.



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2. a) R.M. Buchanan, C. G. Pierpont, *J. Am. Chem. Soc.* **1980**, 102, 4951. b) M. Verdagner, C. Roux, D. N. Hendrickson, *Inorg. Chem.* **1996**, 35, 2846. c) O. Sato, A. Cui, *Acc. Chem. Res.* **2007**, 40, 361. d) H.-C. Chang, *et al.*, *J. Am. Chem. Soc.*, **2008**, 130, 5515 e) H.-C. Chang, *et al.*, *Eur. J. Inorg. Chem.* **2013**, 642.