

Poster Presentation

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Towards Controlling the Valence Tautomer Interconversion Character by Solvation

M. Ribeiro¹, D. Stasiw², D. Shultz², P. Pattison³, P. Raithby⁴, C. Pinheiro⁵

¹Universidade Federal de Minas Gerais, Departamento de Química, Belo Horizonte, Brazil, ²North Carolina State University, Department of Chemistry, Raleigh, United States, ³European Synchrotron Radiation Facility, Swiss-Norwegian Beam Line, Grenoble, France, ⁴University of Bath, Chemistry Department, Bath, United Kingdom, ⁵Universidade Federal de Minas Gerais, Departamento de Física, Belo Horizonte, Brazil

Valence tautomers are bi-stable functional molecular materials in which it is observed charge transference between redox active ligands and a metallic center followed by the change of spin of the metal. Valence tautomerism (VT) interconversion is entropically driven and induced by external stimuli such as irradiation by light and soft X-rays and/or changes in temperature and pressure. VT interconversion is also associated with remarkable variations in optical and magnetic properties and can be modulated with slight chemical changes [1]. Typical examples of valence tautomers are coordination compounds of Co and o-dioxolenes ligands [2]. Crystals of the [Co(diox)(4-X-py)₂], where diox = 3,5-di-t-butylcatecholate/3,5-di-t-butylsemiquinonate, X=CN/NO₂, py= pyridine, were initially studied with respect to low spin (LS) to high spin (HS) thermo and photoinduced VT interconversion. It was reported that [Co(diox)(4-CN-py)₂] crystals become HS-Co³⁺ at temperatures below 110 K with cooperative VT interconversion whereas [Co(diox)(4-NO₂-py)₂] crystals present non cooperative VT interconversion [3]. Toluene and benzene solvates of [Co(diox)(4-NO₂-py)₂] and [Co(diox)(4-CN-py)₂] have been prepared to investigate further the solvation effects on the VT interconversion properties. Analysis of the single crystal X-ray diffraction data obtained during cooling and heating at temperatures ranging from 293 K to 90 K indicated that [Co(diox)(4-CN-py)₂] toluene and benzene as well as [Co(diox)(4-NO₂-py)₂].toluene solvate crystals undergo into non cooperative VT interconversion. The [Co(diox)(4-NO₂-py)₂].benzene crystal show a highly cooperative VT interconversion with a pronounced hysteresis. Intermolecular interactions between inlayer [Co(diox)(4-X-py)₂] molecules are responsible for the VT interconversion in all compounds, however the VT interconversion cooperativity seems to be related with the strength of the Car-H...Odiox interactions and with the correspondent Co-Co separation. Thus solvation plays a key role in the definition of the VT interconversion nature. Acknowledgments: FAPEMIG, CNPq and CAPES grant 10030-12-3.

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