

Structural Properties Of The Valence Tautomerism Interconversion In $\text{Co}(\text{Diox})_2(\text{Py})_2$ Crystals

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This work reports on the investigation of key chemical environmental factors that modulate valence tautomerism (VT) in $\text{Co}(\text{diox})_2(\text{Py})_2$ (diox = 3,5-di-tert-butyl semiquinone and Py = pyridine) complexes. Single crystal X-ray diffraction experiments in a wide range of temperatures have been used to characterize the influence of the crystal packing and solvation in the VT interconversion of $\text{Co}(\text{diox})_2(\text{Py})_2$ pyridine solvated crystals crystallized with complex/solvent ratio of 1:0, 2:1 and 1:2. Our results showed that the mobility of the pyridine, and in particular the rotation of Py plane around the Co-Py bond is directly correlated to the possibility of changes in the electronic states that lead to the Co-N and Co-O distances changes upon the High Spin (HS-Co^{II}) \Leftrightarrow Low Spin ($\text{LS-Co}^{\text{III}}$) VT interconversion. A compilation of literature results also shows a correlation between pyridine-like ligands (PyL) angular distribution and the changes in the electronic/magnetic state of the $\text{Co}(\text{diox})_2(\text{PyL})_2$. For about 50 $\text{Co}(\text{diox})_2(\text{PyL})_2$ structures found in CCDC, the Co-N distances remain constant around 1.95 Å (systems in the $\text{LS-Co}^{\text{III}}$ state) with the increasing PyL rotation angle up to a critical value of $\sim 17.5^\circ$ above which a second linear regime takes place with Co-N increasing up to ~ 2.20 Å (HS-Co^{II} state) when PyL rotation angles range from $\sim 18^\circ$ up to almost 30° . This result highlights the critical role of the so-called innocent ligands in the electronic state of the Co -based VT complexes.