STRUCTURAL AND ELECTRONIC PROPERTIES OF THE VALENCE TAUTOMERISM IN Co(DIOXOLE)$_2$PY$_2$ CRYSTALS

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This study investigates the chemical environmental factors influencing valence tautomerism (VT) in trans pyridine-solvated Co(*dioxolene*)$_2$(Py)$_2$ complexes, where *dioxolene* represents 3,5-di-tert-butyl semiquinone and 3,5-di-tert-butyl catecholate, and Py stands for pyridine [1]. Co(dioxolene)$_2$(Py)$_2$ crystals with complex/solvent ratios of 1:0, 2:1, and 1:2 were analyzed using single-crystal X-ray diffraction across a wide temperature range to understand the influence of crystal packing and solvation on VT interconversion. Our findings show that the orientation of pyridine with respect to the *dioxolene* plane (θ in Figure 1) directly correlates with the possibility of LS-CoIII ⇔ HS-CoII VT interconversion. A survey of Co(*dioxolene*)$_2$(PyL)$_2$ structures in the CCDC [2] also reveals a correlation between θ and the electronic/magnetic state of Co(*dioxolene*)$_2$(PyL)$_2$ complexes. To further understand this effect, we performed DFT calculations in 2:1 complex considering both single molecules and an extended crystalline lattice. The magnetic susceptibility curve as a function of temperature obtained with the LDA functional is in good agreement with experimental results [3]. Indeed the cobalt atoms in solid are borderline, meaning they can change their magnetic state with small changes in the Co-N and Co-O bond distances. The net spin density is centered on Co and decreases monotonically upon cooling on the oxygen atoms of *the dioxolene*. Additionally, the energy associated with LS-CoIII correlates with θ, as suggested by the structure analysis, highlighting the pyridine role in determining the electronic state of Co(*dioxolene*)$_2$(PyL)$_2$ complexes.

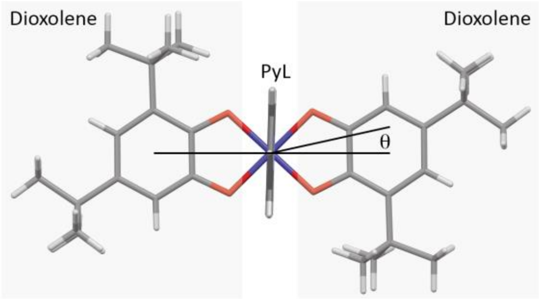

Figure 1: *relative orientation of the pyridine-like ligands in relation to the dioxolene planes*

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References

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