

Poster Presentations

[MS24-P35] Towards Controlling the Valence Tautomer Interconversion Character by Solvation.

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Valence tautomers[1] 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[2], induced by external stimuli such as illumination[3] and/or changes in temperature and pressure[4].

Valence tautomerism (VT) interconversion is essentially entropically driven, associated with remarkable variations in optical and/or magnetic properties, and can be modulated with slight chemical changes. Typical examples of VT compounds are coordination compounds of Co and *o*-dioxolenes ligands[5].

Crystals of complex [Co^{III}(SQ)(Cat)(4-NO₂-py)₂] (**I**), where py= pyridine, Cat = 3,5-di-*t*butylcatecholate and SQ=3,5-di-*t*butylsemiquinonate, were first studied with respect to low spin (LS) to high spin (HS) thermo and photoinduced conversion. It was reported that **I** become HS-Co^{III} at temperatures below 110 K with non cooperative LS-Co^{III} $n \leftrightarrow$ HS-Co^{II} tautomeric interconversion[6]. Crystals of Co^{III}(SQ)(Cat)(4-NO₂-py)₂/Toluene (**II**) and Co^{III}(SQ)(Cat)(4-NO₂-py)₂/Benzene (**III**) have been prepared to investigate further the solvation effects on the interconversion properties. It has been found that solvated crystals undergo to LS-

Co^{III} $n \leftrightarrow$ HS-Co^{II} interconversion at temperatures below 140 K for **II** and below 110 K for **III**. The tautomeric interconversion in **I** and in **II** has a non cooperative character whereas for **III** it is highly cooperative. The remarkable common structural features in the three dimensional packing of compounds **I**, **II** and **III** are the Car-H...O_{diox}ⁱ and Car-H...ONOⁱ hydrogen bonds between inlayer *i* symmetry related [Co^{III}(SQ)(Cat)(4-NO₂-py)₂] molecules with distances values summarized below.

	Distances at <i>ca.</i> 100 K (Å)		
	I[6]	II	III
C-H...O _{diox}	3.24	3.33(2)	3.131(7)
C-H...ONO	3.32	3.34(2)	3.287(7)
¹ Co ^{III} -Co ^{III}	7.283	7.333(1)	6.9491(8)
² Co ^{III} -Co ^{III}	11.788	11.757(1)	12.331(2)
³ Co ^{III} -Co ^{III}	11.718	14.944(2)	15.357(3)

1, 2 and 3 indicate distances between cobalt atoms in molecules linked by C-H...O_{diox}ⁱ, C-H...ONOⁱ and out of layers respectively.

When compared with **I**, the inclusion of the toluene in the lattice of **II** does not affect the symmetry of the crystal structure (**I** and **II** are described by P2₁/c space group, Z=4), but increases the separation between the layers of [Co^{III}(SQ)(Cat)(4-NO₂-py)₂] interacting molecules in *ca.* 30%, weakening the *t*-butyl interactions, as also observed in [Co^{III}(SQ)(Cat)(4-CN-py)₂] compound[7].

Benzene solvated crystals **III** are described by P1 space group, Z=2, and at 100 K. When compared with **I** and **II**, benzene solvated crystals present the shortest C_{ar}-H...O_{diox}ⁱ and similar C_{ar}-H...ONOⁱ hydrogen bonds lengths.

They also present the shortest Co^{III}-Co^{III} distances between inlayer molecules linked by Car-H...O_{diox}ⁱ and the longest Co^{III}-Co^{III} distances between

Thus, as already pointed out before[6], VT in $[\text{Co}^{\text{III}}(\text{SQ})(\text{Cat})(4\text{-NO}_2\text{-py})_2]$ seems to be due to the intermolecular interactions between inlayer molecules, however the interconversion cooperativity seems to be related with the strength of the $\text{Car-H}\cdots\text{O}^i_{\text{diox}}$ interaction and with the correspondent Co–Co_i separation.

Thus solvation play a key role in the definition of the VT interconversion nature.

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