

# Fully fluorinated Pd(F6acac) complexes: polymorphism and fluorine-fluorine interactions.

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Weak intermolecular interactions such as hydrogen bond,  $\pi$ - $\pi$  stacking, and halogen bond, play a crucial role in stabilizing crystal packing and in the formation of polymorphs and supramolecular motifs. Among the weak intermolecular interactions, fluorine-fluorine and hydrogen-fluorine interactions are expected to provide only a small stabilization contribution to the crystal packing and they are often considered non-stabilizing. [1, 2] For this reason, their role in influencing the solid state properties of a compound is still questioned.  $F\cdots F$  short contacts, with  $F\cdots F$  distance shorter than the sum of the VdW radii (2.94 Å), are usually considered a consequence of tight crystal packing. However, there are examples of fluorinated compounds where  $F\cdots F$  interactions are the driving force of the crystal packing, or at least they provide energy stabilization, contributing to the formation of patterns, motifs, and polymorphs. [3, 4]

We present a study on the polymorphism of a fully fluorinated Pd dimer prepared by reaction of palladium bis(hexafluoroacetylacetonate) ( $Pd(F6acac)_2$ ) with pentafluoroaniline (PFA). PFA is deprotonated upon coordination with two palladium atoms, forming a N-bridged dimer (Fig 1.). The PFA ligands in the dimer can either have trans or cis conformation. Due to the presence of 22 fluorine atoms in the dimer, different F-F interactions are possible in the packing, generating polymorphs for both the trans and the cis stereoisomer. In addition to the polymorphs, we also characterized several solvate co-crystals. All the crystal structures observed have multiple  $F\cdots F$  short contacts (2.647 - 2.934 Å). The crystals of the trans complex also undergo a reversible structural transformation from triclinic (P -1) to monoclinic (P 2<sub>1</sub>/c) in the temperature range 220-221 K. The transformation is noticeable as systematic absences corresponding to the 21 screw axes appear at  $T > 221$  K in the diffraction pattern (Fig. 2).

[1] Berger, R. Resnati, G. Metrangolo, P. Weber, E.; Hulliger (2011), *J. Chem. Soc. Rev.* 40, 3496.

[2] Panini, P. & Chopra, D. (2015) *Hydrogen Bonded Supramolecular Structures*, edited by Z. Li and L. Wu, vol. 87, Springer.

[3] Bayón, R. Coco, S. Espinet, P. (2005) *Chem. Eur. J.* 11, 1079.

[4] Mariaca, R. Behrnd, N.-R. Egli, P. Stoeckli-Evans, H. Hulliger, J. (2006), *CrystEngComm*, 8, 222.

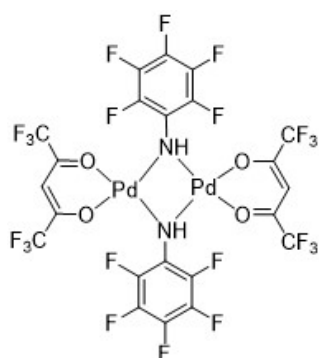


Figure 1

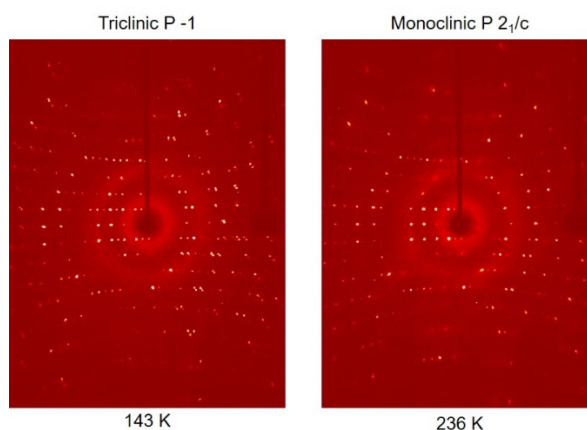


Figure 2