

4-membered Metallodithiophosphinate Rings – Flat or Puckered?

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During the preparation of the complex (diphenylphosphinodithiolato)(phenyl)(triphenylphosphine)-palladium(II) ($C_{36}H_{30}P_2PdS_2$) it was found that two crystalline forms were obtained from two different solvent mixtures: one without solvent, the other containing THF (C_4H_8O). Single crystal X-ray diffraction analysis showed that the molecular structures differed in the planarity of the 4-membered palladium dithiophosphinate rings, with the complex in the crystal containing solvent taking on a flat conformation, whereas in the crystal without solvent the ring is planar. In order to explain these results the experimental conformations were compared to the conformations of 4-membered metal-S₂P rings reported in the Cambridge Structural Database (CSD) [1], where it was shown that a flat conformation is more common than a puckered one. DFT calculations at the B3LYP level of theory indicate that the flat conformation of a model metallodithiophosphinate ring is very slightly lower in energy (1.2 kcal/mol) than the puckered conformation, thus supporting the CSD analysis. Closer investigation of the crystal packing shows that the puckering can be traced back to weak off-set face-to-edge π - π interactions between one of the phenyl rings in the diphenyldithiophosphinate ligand and phenyl rings in the neighbouring molecules.

[1] Allen F.H., *Acta Cryst.*, 2002, B58, 380.

Keywords: conformation rings, intermolecular interactions, computer simulation of structure