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Supramolecular arrangements of titanium dichloride ketimide complexes with Cp type ligands

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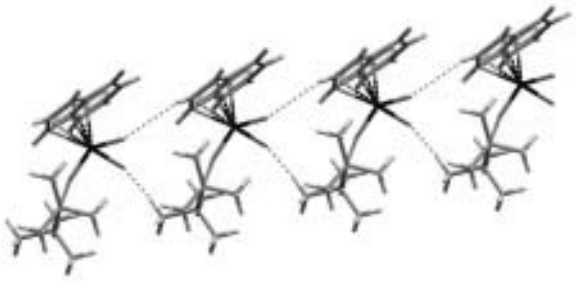
The packing in titanium dichloride ketimide complexes with cyclopentadienyl type ligands is strongly dependent on the interactions formed by the two chloride ligands. In this study we report the influence in these interactions and the resulting supramolecular arrangements of the presence of different substituents in the Cp ring and also in the ketimide ligand. Both the characteristics of the individual molecules and the optimization of the intermolecular interactions result in supramolecular arrangements that range from the conventional 3-D arrays to more organized packings like linear and helicoidal chains. In this work we use our own crystallographic results [1] together with data retrieved in CSD [2].



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Supramolecular cocrystallisation: a new paradigm for the organic solid state

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Supramolecular synthesis of new types of cocrystals promises to extend the known collection of crystalline materials[1]. Crystal engineering as a type of supramolecular synthesis[2] finds applications in a variety of fields, while an enhanced database regarding supramolecular synthons will facilitate and provide information increasing our understanding, ultimately leading the way to rational design. Cocrystallising substrates and performing reactions in the solid state is an active area of research providing new approaches to carefully control the regio- and stereoselectivity of reactions and solvent-free organic synthesis - green chemistry - offers many advantages. The rational design of cocrystals through crystal engineering is of particular importance to the pharmaceutical industry as improved properties for pharmaceutical materials may be afforded. Relevance of crystal engineering also stretches to possibilities of novel industrial heterogeneous catalysts as well as storage matrixes for gases such as hydrogen and methane. Cocrystals are usually a result of simple mixtures of components on a molecular scale. Herein we describe the solid state structure of a cocrystal on a supramolecular level, where the cocrystal is sustained entirely by noncovalent forces. Dianin's compound (4-*p*-hydroxyphenyl-2,2,4-trimethylchroman) has been known for almost a century. Its inclusion behaviour has been studied almost as long and many crystal structures with the compound as host have been reported. The racemate of Dianin's compound typically crystallises with six molecules around a site of $\bar{3}$ symmetry to form a hexameric O-H•••O hydrogen bonded cyclic arrangement. The hydrogen bonded ring is constituted by the phenolic hydroxyl groups of alternating *R*- and *S*- stereoisomers, with three molecules situated above the hydrogen bonded ring and their three enantiomers positioned below the plane. In a structure previously reported by our group, a new form of Dianin's compound hosting morpholine has been described in which the established structural consistency is perturbed [3], resulting in a slightly different supramolecular motif. We have now found yet another deviation from the well-recognized archetype of the host molecule. When the host is crystallised with ethylene diamine, a third crystal form is observed, consisting of a combination of the two reported supramolecular motifs for this system, thus illustrating the concept of supramolecular cocrystallisation, a new paradigm for the organic solid state.

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