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New low-melting molecular complexes of common solvents - crystallization, structures, packing motifs

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The structural studies of low-melting molecular complexes (LmMC), i.e. co-crystals of components which are liquid under ambient condition, attract a lot of interest in recent years [1]. These complexes are usually formed by small molecules and thus provide excellent models for theoretical chemistry as the number of possible intermolecular interactions in such systems is low.

Earlier [2] we reported crystallization and structures of several LmMC of chloroform (CF) and dichloromethane (DCM) with small cyclic ketones and amines. In continuation of these studies several new LmMC of common organic solvents such as acetone, DMSO butanone-2 with CF, DCM and 1,2-dichloroethane have been grown *in situ* on a diffractometer and structurally characterized. The obtained crystal structures are compared with the structures of pure components and of previously known LmMC. In spite of seeming simplicity of the components, the structures display a variety of types and motifs of intermolecular interactions. Alongside with (C)C-H...O contacts, which are present in all studied structures, a number of other weaker interactions have been observed. Fine balance of these interactions and different spatial arrangements of the "syntons" make such LmMC unique, curious and challenging for prediction. However it is possible to outline general tendencies and make some conclusions about the driving forces of crystallization of LmMC. Attempts to use them in the design of co-crystallization experiments will also be discussed.

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The Multiple Phenyl Embrace: a useful synthon in crystal engineering

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The Multiple Phenyl Embrace (MPE), first described in 1995 by I. Dance and M.L. Scudder, [1] is a supramolecular motif comprised of phenyl rings involved in multiple aromatic interactions, which can, like hydrogen bonds, form extended networks between molecules in the solid state. The MPEs are of a strong attractive nature and they could, therefore, dominate solid state structures, which might lead to the formation of networks in one, two, and three dimensions.

Our MPE analysis focuses on crystal structures of coordination

polymers based on a Cu(I)/PPh₃/N-donor ligand system. [2] By varying the linker ligand (pyrazine, 4,4'-bipyridine and 3,4'-bipyridine), anion (X = BF₄⁻, ClO₄⁻ and PF₆⁻) and solvent (CH₂Cl₂, CHCl₃, THF) a series of coordination polymers was synthesized resulting from reactions with [Cu(MeCN)₂(PPh₃)₂][X] as starting material. The 18 crystallization experiments with linear N-donor ligands yielded seven crystal structures of 1D and five crystal structures of 2D coordination polymers. The nine crystallization experiments with the non-linear N-donor ligand yielded four crystal structures showing 1D coordination polymers. [3]

The first stage of our analysis comprises the search for intermolecular P-P distances and M-P---P-M colinearities, which are parameters that can identify the presence of a Multiple Phenyl Embrace. The second stage is to describe the intramolecular geometry of the PPh₃ group, which tells us something about the strength of the embrace.

The analysis of 23 crystal structures, 16 from the 27 crystallization experiments mentioned above and 7 comparable ones from literature, [4] showed that 71% of the independent M-PPh₃ groups are involved in a six-fold phenyl embrace (6PE). Strong 6PE interactions are obtained when the geometry of the PPh₃ group can be described as a rotor. The analysis of these groups showed that 83% of the PPh₃ groups have their phenyl groups in the rotor conformation. It is shown, however, that these good rotors are not necessarily involved in the 6PE, and that the 6PE can also be formed by non-rotors.

In the Cu(I)/PPh₃/N-donor ligand system the 6PE interactions form an independent connection (often) perpendicular to the backbone of the coordination polymer. In many cases the 6PE increases the dimensionality of the network formed between Cu(I) and N-donor ligands. Therefore, the Multiple Phenyl Embrace seems to be a useful synthon in crystal engineering of stable networks.

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Impact of metal coordination on amide synthons in picolinamide complexes

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Due to the abundance of the amide functionality in biological systems, the structural chemistry of the amide moieties has received considerable attention. The supramolecular behaviour of the amide functionally in organic systems is well characterized. It has become clear that it is robust and reliable supramolecular connector. It links discrete organic molecules through supramolecular R²₂(8) synthons at high supramolecular synthetic yield. However, relatively little work has been done in constructing predictable architectures of coordination compounds [1]. Picolinamide, having a carboxamide moiety in *ortho* position, distinctly to the other two of its isomers acts as chelating ligand, mostly through *N,O* donor set of atoms, thus imposing some restrictions on accessibility of the amide group for participation in hydrogen bonding [2], [3], [4]. The search of the CSD, confined to octahedral chelating-*N,O* dipicolinamide complexes, revealed that tetrameric motif [R²₄(8)] is more commonly found than the dimeric one [R²₂(8)]. Particularly, the dimer is observed in only one, while