

coefficients as determined from variable temperature x-ray diffraction. Molecular dynamics is used to fully characterise ligand movement, and understand the extend to which framework flexibility determines mechanical behaviour.

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Keywords: metal-organic frameworks, flexibility, molecular dynamics

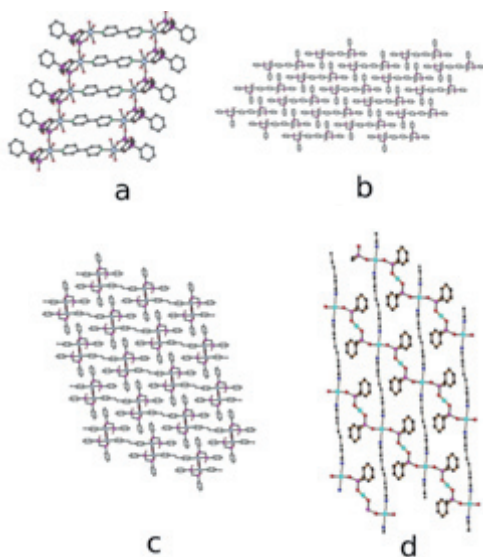
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Polymer dimensionality lead by supramolecular interactions in cobalt system

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Supramolecular forces are involved in the building of the three-dimensional structure in the solid state [1]. Few years ago, it has shown that in metal inorganic organic hybrids the metal coordination environment can be forced by non-covalent interactions. The close packing of 2,2'-bipyridine ligands was responsible for the uncommon trigonal prismatic coordination of Mn(II). The normal octahedral Mn(II) coordination was restored when the intercalation of the bipyridine was prevented using substituted bipyridines [2].



We report here a series of hybrid inorganic organic polymers $[\text{Co}(\text{pcp})(4,4'\text{-bipy})_{0.5}2\text{H}_2\text{O}]_n$ (**1**), $[\text{Co}(\text{pcp})(\text{bpye})_{0.5}\text{H}_2\text{O}]_n$ (**2**), $[\text{Co}(\text{pcp})(\text{bpyet})_{0.5}\text{H}_2\text{O}]_n$ (**3**) and $[\text{Co}(\text{pcp})(\text{bpyet})_{0.5}]_n$ (**4**) where pcp = P,P'-diphenyl-methylene-diphosphinato, 4,4'-bipy = 4,4'-bipyridine, bpye = 1,2-bis(4-pyridyl)ethane, bpyet = 1,2-bis(4-pyridyl)ethene).

In Figure 1 are shown 1D ribbon in **1** (a) and the packing view of **1** (b) and of **2** (c) parallel to the ribbon, finally the packing view of **4** (d).

In the 1D polymer of **1**, the ribbons of $[\text{Co}_2(\text{pcp})_2\text{bipy}]_n$ are connected by hydrogen bonds (Figure 1a and 1b) while **2** and **3** are built by 2D plane formed by the same kind of 1D ribbons that are covalent bonded by water molecules. The view of the packing parallel to the ribbons shows the same type of arrangement of the phenyl rings

of pcp and of the bi-pyridines. For **4**, a totally different 2D network was found with 1D columns of $[\text{Co}(\text{bpyet})]$ connected by square planar $\text{Co}(\text{pcp})_2$ units (Figure 1d). The role of the bipyridine and its length in the formation of the network will be discussed.

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Keywords: metallorganic polymers, diphosphinate, supramolecular chemistry

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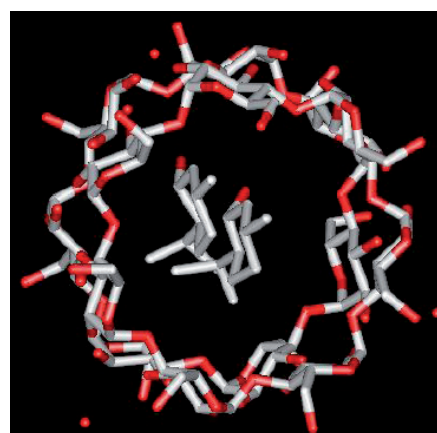
Inclusion Complex of β -Cyclodextrin and l-Menthol

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Cyclodextrins are the cyclic oligosaccharides composed of the glucopyranoses linked by α -1,4-glucoside bond. There are three common cyclodextrins with 6, 7 or 8 D-glucopyranosyl residues, α -, β - and γ -cyclodextrin respectively. Cyclodextrin has the truncated corn shape with hydrophilic OH substituents outside and hydrophobic cavity inside the molecule. The secondary alcohols (2-OH and 3-OH) make bigger and primary alcohols (6-OH) make smaller rims of truncated corn structure. Therefore, cyclodextrin can include the water insoluble molecules inside its cavity. This property is applied for various reagents to solubilize in water, stabilize from oxidation, recognize a molecule, or transfer a drug. Menthol has local anesthetic and counterirritant qualities, and it is widely used to relieve minor throat irritation. Menthol is included in many products such as toothpaste, chewing gum, cigarette etc. To keep the function of menthol, cyclodextrins are often included in these products. In order to understand the molecular function of cyclodextrin in these products, the crystal structure of β -cyclodextrin and l-menthol was determined by the X-ray diffraction method.

The inclusion complex of β -cyclodextrin and l-menthol crystallized in monoclinic space group $P2_1$ with cell parameters of $a=15.2487(7)$, $b=32.487(1)$, $c=15.3835(5)\text{\AA}$, $\beta=101.712(1)^\circ$, $V=7462.2(5)\text{\AA}^3$, $Z=2$, $F.W.=2582.52$. Two β -cyclodextrins and two l-menthols are in the asymmetric unit. The X-ray diffraction data were collected on Rigaku RAPID diffractometer. The crystals include many crystalline waters and were very unstable in air. Thus, the data measurements were carried out at -150 deg. using flash cooling method. In total, 33,583 independent reflections were observed ($R_{int}=0.0293$). Crystal structure was solved by direct method (SHELXD) and refined by full-matrix least-squares on F^2 (SHELXL-97). The present $R1$ is 0.1100.

The crystal structure is shown in the figure. Two



The detailed molecular interactions between β -cyclodextrin and l-menthol will be discussed.

β -cyclodextrins make a dimer facing bigger rims to each other. Inside the dimer, two l-menthols are included with their molecular axes in the same direction.

Keywords: inclusion complex, β -cyclodextrin, l-menthol

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Self-assembly of metal trischelates to afford extended structures for porous applications

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The search for porous materials and design principles to achieve this aim is ever increasing. These materials have a variety of potential applications such as catalysis, gas separation and storage. Problems that exist in the assembly of porous materials are the tendency of molecules to pack closely in the solid state, thereby obliterating free space. In recent years the use of polymeric metal-coordination compounds for porous applications has increased with the realisation that judicious choice of metal centre and rigid bridging ligand can afford two- and three-dimensional solids that feature the desired characteristics [1, 2, 3]

Work will be presented where octahedral trischelate complexes based on functionalised 2,2'-bipyridine ligands are linked into two- and three-dimensional networks using a variety of supramolecular interactions. The stability of these crystalline materials toward evacuation and solvent-loss will be shown, as well as their permeability to gasses as proven by gas sorption.

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Keywords: self-assembly, supramolecular, bipyridine

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Novel coordination polymers based on rigid and flexible organic ligands and Cu(II) ions

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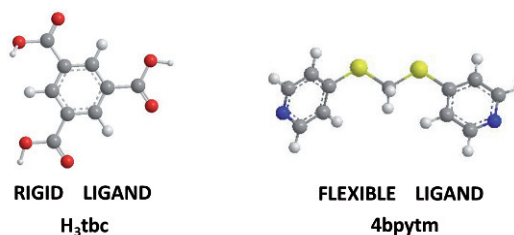
Dynamic polymers based on monomeric components connected through either labile noncovalent interactions or reversible covalent bonds, are the subject of intense investigation. [1] A special class is formed by coordination polymers, where the control of the polymerization is made through metal-ion coordination bonds. In addition, the presence of noncovalent interactions along the polymeric backbone results in that the material could exhibit reversible polymerization/depolymerization properties. [2] Many of the architectures reported to date are based upon rigid linear linker ligands, with less efforts focusing on the use of ligands showing conformational flexibility. The use of flexible ligands can lead to the formation of interesting architectures without loss of control in the self-assembly process.

We have performed an investigation on the formation of copper(II) coordination compounds based on the use of the 1,3,5-benzenetricarboxylic acid (H_3btc) and the spacer with conformational

flexibility, bis(4-pyridylthio)methane (4bpytm). As result of this study two new coordination polymers are prepared and characterized: $^1_\infty[Cu(H_2btc)_2(4bpytm)]$ (**1**) and $^2_\infty[Cu(Hbtc)(4bpytm)_2] \cdot H_2O$ (**2**). Both compounds are obtained as a mixture by a solvothermal procedure. The optimization of the synthetic route allowed the isolation of the pure phases in a high yield.

The 1D covalent network (**1**) is achieved by the bridging role of 4bpytm ligand between the copper(II) ions, with the biprotonated H_2btc^- ligand acting as terminal ligand. 4bpytm produce also chains in (**2**) that are further pillered by the monoprotinated ligand $Hbtc^-$ to form high robust layers. An interesting feature is that in both compounds exist different open sites per copper atom that form coordinatively unsaturated metal centres (UMCs) that can strongly interact with guest molecules. The use of a ligand with carboxylate groups partially protonated makes that the corresponding supramolecular associations are organized by the effect of different OH...O hydrogen bonds.

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Keywords: copper complexes, crystal structures, metallosupramolecular chemistry.

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Structural studies and electron density analysis of thiophene based compounds

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As the galloping energy demands of the world combined with the environmental concerns call for looking alternate and cleaner sources of energy, much attention is being diverted to the renewable sources of energy, including the solar energy. Dye sensitized solar cells (DSSCs) are proving to be a potential alternate for the conventionally used semiconductor based solar cells [1]. They offer many advantages such as tuneable electronic properties, especially the band gap, by chemical modifications and substitutions. In this context, thiophenes and their substituted homologues have attracted much attention of the scientific community as the starting materials for the synthesis of organic dyes and metal organic complexes worth applicable in DSSCs. It is considered that the backbone retains its π -conjugated coplanar conformation if the long alkyl chain is substituted at a suitable