

to control polymorphism in pharmaceuticals. Our compound of interest is pyrazinamide (PZA), a polymorphic API used in the treatment of tuberculosis and is known to exist in 4 different forms. Only two cocrystals of PZA have been reported to date. We identified aminobenzoic acid (ABA) and hydroxybenzoic acid (HBA) as suitable cocystal formers (coformers) for PZA. In addition, we decided to investigate the effect of changing the orientation of the hydrogen bonding groups in ABA and HBA on cocystal formation by employing the 3 constitutional isomers of each for a total of 6 coformers: *o*-aminobenzoic acid (*o*ABA) commonly known as anthranilic acid, *m*-aminobenzoic acid (*m*ABA), *p*-aminobenzoic acid (*p*ABA), *o*-hydroxybenzoic acid (*o*HBA) commonly known as salicylic acid, *m*-hydroxybenzoic acid (*m*HBA) and *p*-hydroxybenzoic acid (*p*HBA). Our results show that PZA forms a cocrsytal with each of the coformers, repeatedly and consistently suggesting that they are not polymorphic. This presentation will show the synthesis and characterization of 6 new PZA cocrystals, namely PZA•*o*ABA (1), PZA•*m*ABA (2), PZA•*p*ABA (3), PZA•*o*HBA (4), PZA•*m*HBA (5) and PZA•*p*HBA (6). The characterization techniques employed include powder X-ray diffraction (PXRD), differential scanning calorimetry (DSC), melting point, and in some cases <sup>1</sup>H NMR and single crystal X-ray crystallography (cocrystals 1 and 3).

**Keywords:** cocrystal, polymorphism

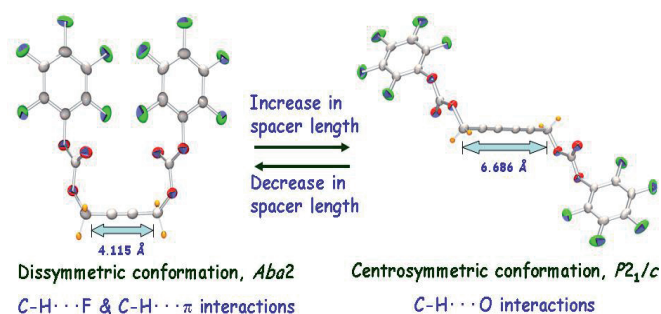
## MS24.P30

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### 'Organic' fluorine dictates the molecular conformation and packing

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Fluorinated compounds have gained an immense importance because of their role in day-to-day life [1]. The chemical, physical and biological properties of these compounds have been well-recognized in terms of interactions involving fluorine. The robustness of C–F···H, F···F and C–F···π interactions can be exploited in controlling the conformational features and supramolecular structural organization of the conformationally flexible molecules [2]. In this context, the crystal structures of three aryl biscarbonates and an aryl biscarbamate namely, But-2-yne-1,4-diyl bis(2,3,4,5,6-pentafluorophenylcarbonate), 1; But-2-yne-1,4-diyl bis(4-fluorophenylcarbonate), 2; But-2-yne-1,4-diyl bis(2,3,4,5,6-pentafluorophenylcarbamate), 3 and Hexa-2,4-diyne-1,6-diyl bis(2,3,4,5,6-pentafluorophenylcarbonate), 4 with rigid acetylenic unit providing variable spacer lengths have been analysed [3]. Compound 1 adopts a noncentrosymmetric 'twisted' (syn) conformation, whereas 2, 3 and 4 acquire a centrosymmetric 'extended' (anti) conformation, a commonality of such molecules as revealed by Cambridge Crystallographic Database search results. Weak intermolecular interactions and in particular those involving fluorine [C<sup>sp3</sup>–H···F–C<sup>sp2</sup>] are found to dictate this conformational variation in the crystal structure of 1. Neutron diffraction study at 90 K was performed on 1 to obtain further insights into these interactions involving 'organic' fluorine. We demonstrate that the conformational preferences and the supramolecular organization in the crystal lattice adopted by aryl biscarbonates 1, 2 and 4 and an aryl biscarbamate, 3 are the consequence of a counterbalance between the molecular symmetry and the weak intermolecular interactions involving the 'organic' fluorine.



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### Structural studies of selected photochromic compounds

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Photochromic compounds displaying property changes upon conversion are of interest for potential applications including optical switching devices and memory media. Anils, Schiff bases of salicylaldehyde derivatives with aniline derivatives, exhibit both solid-state thermo- and/or photochromism through an enol-keto tautomerism mechanism. The final thermoproduct is the *cis*-keto form whereas the photoproduct is the *trans*-keto form [1]. These compounds show potential for "crystal engineering" because their properties are greatly influenced by their surroundings. Hence, by altering substituents, adding bulky groups to increase lattice "space" or by making inclusion compounds, thermo- and/or photochromic properties can be enhanced towards specific applications [2].

To examine structure-property relationships various substituted anils have been synthesized and studied using Raman spectroscopy, crystallographic methods and diffuse reflectance spectroscopy [3]. All the compounds investigated display some degree of thermochromism. The strongly thermochromic compounds show a large visible colour change from orange/red at room temperature to yellow in liquid nitrogen but rarely display photochromism. Some of the weakly thermochromic compounds are also photochromic, changing from yellow to orange/red upon UV irradiation and reverting back to their original colour thermally or upon irradiation with visible light ( $\lambda > 560$  nm). Molecular planarity is thought to be disfavoured for photochromism but in this study several anil compounds with *interplanar* angles of  $< 10^\circ$  have been found to display distinct colour change upon UV irradiation.

It is suggested that the thermo- and/or photochromic properties displayed depend on a complex interplay of factors determined by the type of substituents, the molecular and packing structure, in particular *interplanar* angle, *intermolecular* interactions, void space around the central imine group and possibly other influences.

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2005, 6, 207-226. [3] T. Fujiwara, J. Harada and K. Ogawa, *Journal of Physical Chemistry B* **2004**, 108, 4035-4038.

**Keywords:** photochromism, thermochromism, solid-state

## MS24.P32

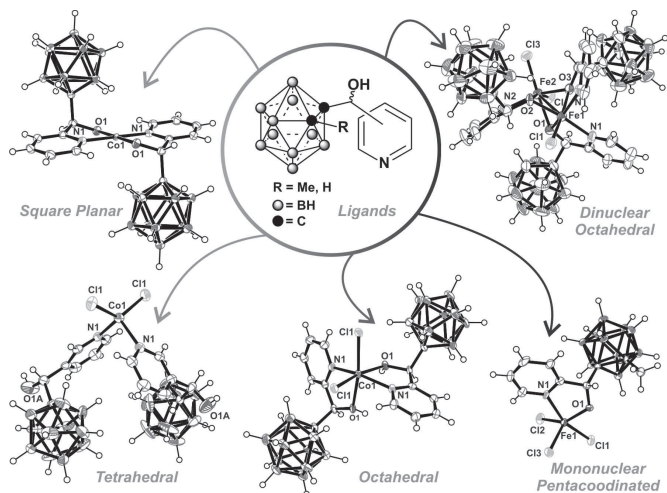
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### Structure and properties of *o*-carboranylalcohols pyridines metal complexes

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The recently reported series of *ortho*-carboranymethylalcohols bearing pyridine substituents [1] opens a new door to the synthesis of very attractive carborane based transition metal complexes (Figure). The two different functionalities (OH and N) together with the chance to vary the nitrogen position along the aromatic ring, the metal, as well as the hydrophobic icosahedral heteroborane cluster, give place to compounds which exhibit different structural architectures and properties.

When an ethanolic or acetone solution of *ortho*-carboranymethylalcohol pyridine or quinolyne derivatives is mixed with a solution containing the desired metallic ion, the corresponding complex is obtained. For instance, for Co(II), the 3- and 4- pyridine and 4-quinoline derivatives give place to tetrahedral geometries whereas the 2-pyridine ones, due to the carboranylalcohol acting as a N, OH/O bidentate ligand, conducts to octahedral or square planar complexes (Figure). On the other hand, when Fe(III) and the 2-pyridine ligands are employed, different structures are obtained depending on the carborane substituents (R in the Figure). For R = H, a pentacoordinated mononuclear complex crystallized as a result of the reaction while for R = Me, an iron dinuclear compound with three oxo bridges is obtained (Figure). Magnetic measurements of the Co complexes are in agreement with their different structures and in the particular case of the octahedral complex, the negative sign of  $\theta$  indicates antiferromagnetic interactions among the monomeric units and matches well with the number of OH...Cl hydrogen bonds found in the crystal structure.



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**Keywords:** crystal engineering, magnetic properties, heteroborane clusters

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### Crystallographic study of labile systems: Cobalt and lawsone complexes

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Bi-stable molecular systems presenting mixed valence (MV), spin crossover (SC) and valence tautomerism (VT) are associated with the development of new functional materials which can be used for applications in organic electric conductors, optoelectronic and molecular magnets [1]. The properties of these materials can be adjusted with little chemical changes or as a response to changes of external parameters such as pressure, temperature and illumination [2]. In VT compounds in particular, the electronic transfer is associated with the change in the electronic and spin properties of the metal [3]. The electronic transfer can be evidenced by the change in the metal-ligand bond length [4] or in some cases only in the bond lengths within the organic ligand. Typical examples of such systems are coordination compounds of Co and ligands like quinonas [4].

Few works investigating the electronic transfer in compounds formed by naphthoquinones and transition metal ion have been reported so far. The results concerning electron transfer in this compounds are discordant [5,6].

In this work we present synthesis and characterization of  $[\text{Co}(\text{Law})_2(\text{Im})_2] \cdot \text{C}_6\text{H}_5\text{CH}_3$ ,  $[\text{Co}(\text{Law})_2(\text{Phen})_2] \cdot (\text{C}_4\text{H}_8\text{O})_2$ ,  $[\text{Co}(\text{Law})_2(2,2\text{-Dipy})]$  and  $[\text{Co}(\text{Law})_2(2,2\text{-Dipy})] \cdot \text{C}_6\text{H}_5\text{CH}_3$ , where Law stands for 2-hydroxy 1,4 naphthoquinone or Lawsone Crystals were isolated after evaporation or slow cooling of solvents and later characterized with elementary analysis, atomic absorption and IR spectroscopy. Single crystal X-ray diffraction experiments performed in the temperature range between 120 K and 150 K allowed the structural determination of compounds. The average bond lengths for Co-N (2,10(2) Å) and Co-O (2,10(6) Å) found in all investigated structures are typical of  $\text{Co}^{\text{II-L}}$ . The typical bond lengths for  $\text{Co}^{\text{III-L}}$  in the systems that present electron transfer should be 0.1-0.15 Å shorter than  $\text{Co}^{\text{II-L}}$  bond length [4]. Furthermore the C=O length value (1,22(1) Å) suggests a double bond in naphthoquinone [7]. Thus, in the investigated temperature range, the X-ray diffraction results did not show any evidence of charge transfer between Co- naphthoquinone.

The compound  $[\text{Co}(\text{Law})_2(2,2\text{-Dipy})]$  formed both a unsolvated and a solvated structure with toluene. The solvated structure crystallizes in triclinic symmetry while the unsolvated crystal structure is orthorhombic. A number of weak intermolecular interactions like  $\text{C}_{\text{ar}}\text{-H}\cdots\text{O}$  can explain the difference in the crystal packing.

Additional X-ray diffraction as well as spectroscopy studies at temperatures down to 10 K will be performed to investigate the presence of electron transfer in Co- naphthoquinone complexes.

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**Keywords:** valence tautomerism, naphthoquinones, cobalt complexes