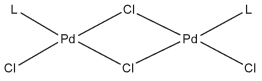
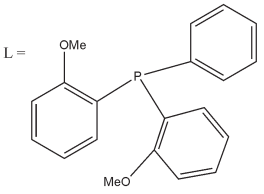
agents [2]. However, the information on the regioselectivity of the corresponding reaction of simple α-olefins is fragmentary, particularly with regard to branched chain selectivity.

Our approach to the synthesis of methyl methacrylate [3], an important monomer in the polymer industry, requires the efficient conversion of propene into methyl-2-methylpropionate as a key step. This has been achieved as part of an ongoing study [4] of the methoxycarbonylation of α-olefins. A detailed kinetic study indicated the dependence of reaction rate on pressure, temperature, solvent polarity, acidity, etc. In addition the results indicated the separation of the rate determining step and the step in which the regioselectivity is established. This selectivity appears to depend on the competition between Markovnikov and anti-Markovnikov addition of Pd–H to α-olefins [5], which is critically dependent on solvent polarity and ligand (triarylphosphine) structure (both steric and electronic).

Structure determination by single-crystal X-ray diffraction of several catalytic precursors [6 – 9] (one such example is compound **I**) has been carried out and has provided much insight into the relationship between reaction mechanism and selectivity and this work focuses on these structure/activity relationships.



Compound **I**



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Keywords: carbonylation catalysis, α-olefins, single-crystal X-ray diffraction

MS31.P21

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Hydrothermal synthesis of 3D mixed sulfate-succinate MOFs

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In previous works, the synthesis of succinates of rare- earth has been carried out to find 2- and 3D MOFs with different properties such as catalytic activity, optical and magnetic properties [1].

Here we report four novel compounds **$[Ln_2(C_2H_4C_2O_4)_2(SO_4)(H_2O)_2]$** [Ln = La (1), Pr (2), Nd (3) and Sm (4)] hydrothermally synthesized and characterised by single crystal X-ray diffraction, powder X-ray diffraction, IR spectroscopy and thermal analysis (TGA). The crystalline products are a series of isostructural 3D polymeric compounds that crystallize in the monoclinic system, space group P2(1)/n. The compounds are formed by dimeric building blocks of trivalent lanthanide cations nona-coordinated linked by the succinate ligand, which acts as oxo-carboxylate bridge in *b* direction and links the metallic chains in *c* direction. The layers are linked in *a* direction by the sulfate anion and a slightly twisted succinate ligand. The use of the sulfate anion as tetradentate ligand (μ_4 η^2) allows the formation of a mixed compound with 3D structure. The presence of the sulfate ligand and strong intramolecular hydrogen bonds contribute to stability of these compounds in comparation with analogues hydrates, as may be seen in the thermal analysis.

1-4 were tested in the hydrogenation of nitro group in aryl derivates obtaining excellent activity and selectivity.

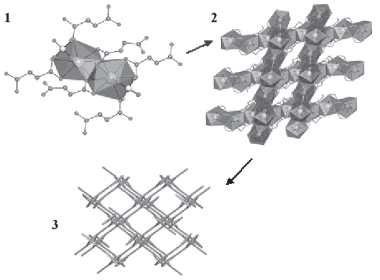

Fig 1. Building block of the isostructural compounds (**1**) and tridimentional representations (**2, 3**).

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Keywords: lanthanide MOFs, Sulfate-succinate, Heterogeneous catalysis

MS31.P22

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A rod packing Zn MOF: acid catalyst in multicomponent reaction (MCR) and topology

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Following the previous studies of our group we used 4,4'-(hexafluoroisopropylidene)diphthalic anhydride as a flexible ligand in order to achieve new topologies in MOFs. By hydrothermal synthesis we have obtained a new Zn MOF with composition $[Zn_3(H_2O)(C_{19}O_8H_7F_6)](H_2O)_{0.33}$ **(1)**. Its structure has been solved from single crystal X-Ray diffraction data. According with rod packing classification, the topological type for the net of **(1)** is **eta.** It is a chiral and uninodal 3-connected net. The final topology is characterized by the Schlafli symbol: $\{8^3\}$, vertex symbol with circuits: [8.8.8(2)]. Topological classification was done with TOPOS[1] and optimized with SYSTRE[2].

This Zn MOF has been tested as acid catalyst in a multicomponent reaction, and its activity is compared with the corresponding for different Zn MOFs with the same ligand [3,4].

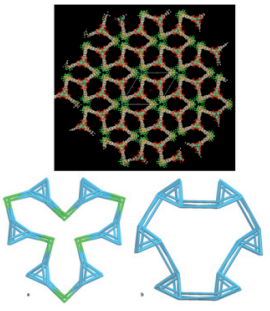

Figure 1 up: Crystal Structure of $[Zn_3(H_2O)(C_{19}O_8H_7F_6)_2](H_2O)_{0.33}$, **down:** topology of decorated net (**a**), not decorated net (**b**).

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Keywords: MOF, topology, MCR-reaction.

MS31.P23

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Crystal Structure of the CcbJ Methyltransferase from *Streptomyces caelestis* [1]

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CcbJ is an S-Adenosylmethionine (SAM) dependent methyltransferase from *S. caelestis* which catalyzes the final step in the biosynthesis of the antibiotic celesticetin. *S. caelestis* has exhibited the ability to synthesize different derivatives of celesticetin depending on the presence of different salicylic acid derivatives in the growth medium. [2] In order to understand how this organism is able to manage this, we have isolated, overexpressed, and purified the individual components of this pathway, including CcbJ [3].

The crystal structure of free CcbJ was determined by Multiwavelength Anomalous Dispersion and that of the CcbJ–SAM complex was determined by molecular replacement (using the free structure as the search model). In both structures CcbJ crystallized in the $C222_1$ space group with unit cell lengths of a = 168.02, b = 244.55, and c = 117.85. In both crystals, the asymmetric unit contained six monomers arranged as a dimer of trimers.

CcbJ possesses the class I SAM-dependent methyltransferase fold [4], [5]; modifications to the core fold include insertion of a four-stranded β-sheet, which serves as an active site cover, between αE and β5 and a short 3_{10} helix between β4 and αD, which forms part of the SAM binding cleft. There is also an extension to the N-terminus. These insertions match the general pattern seen in other small-molecule methyltransferases. Overall, CcbJ appears to be most similar to glycine N-methyltransferase (GNMT) which also has a similar active site cover and a 3_{10} helix in the SAM binding cleft. Aside from a similar overall shape, the active site of CcbJ is quite different from that of GNMT, having a much larger number of aromatic residues.

One of the most characteristic features of CcbJ is the great degree of flexibility exhibited by the residues in the N-terminal extension preceding αZ. In the free CcbJ structure, these residues were completely disordered in one of the six chains and none of the residues preceding Tyr-17 were visible. In the CcbJ–SAM complex, however, the entire extension was visible in all six chains. The newly ordered residues form an α-helix which passes between the active site cover and αB and forms part of the SAM binding site. Following this helix, the extension passes over part of the active site opening before entering helix αZ. The loop between these two helices contains several proline and glycine residues and is likely to be natively unstructured. This would probably allow it to adopt several different conformations which might allow it to accommodate the several different substrates observed *in vivo* [2].

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Keywords: antibiotic, flexibility, methylation

MS31.P24

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1 and 2-D metal-organic polymer of Sc(III) with sufonate-carboxylate ligand

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Reaction of scandium chloride with 3,5- disulfobenzoic acid[1] under hydrothermal conditions leads to the formation of two metal-organic polymer compounds **$[Sc_3(3,5\text{-}DSB)_2(HO)_3(H_2O)_2]$** (**1**) and **$[Sc_3(3,5\text{-}DSB)_2(HO)_2(H_2O)_2]$** (**2**) that crystallize in the triclinic space group P-1. In both cases, the oxygen atoms of the carboxylate group are linking two metallic centers in $\mu_1\,\mu_1\,\eta^2$ mode. Two hydroxyl groups act as bridges linking scandium (III) cations along [011] direction. In the axial positions the scandium is coordinated by the oxygen of the sulfonate group, which is in *anti* coordination $\mu_1\,\eta^1$ mode. Two water molecules are coordinated in equatorial and axial positions. This arrangement allows the formation of bidimentional polymeric structure arranged in layers along (100) plane. The difference between the compounds **1** and **2** is the substitution in the compound **2** of one bridge hydroxyl molecule by one oxygen atom of the sulfonate group ($\mu^1\,\mu^1\,\eta^2$) along the [011] direction.

The utilization of a auxiliary ligand 1,10-Phenanthroline[2], under conditions similar to previous leads to formation of **$[Sc(3,5\text{-}DSB)(Phen)(H_2O)]\cdot(H_2O)$.** In this compound the Sc(III) is hepta-coordinated by the phenathroline chelate, one water molecule and a carboxylate group in $\mu_1\,\mu_1\,\eta^1$ mode in equatorial position and with two sulfonate groups (*anti* $\mu^1\,\eta^1$ mode) in axial position. The *trans* disposition of the ligand allows the formation of polymeric chains that grow along the *c* axis in "ladder" form. The chains are linked by hydrogen bonds along *b* direction; π-π slipped stacking interactions between the rings of the phenanthroline give rise to 3D supramolecular structure.

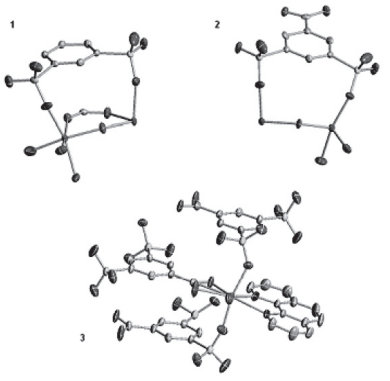

Fig 1. ORTEP drawing of the asymmetric units for **1-3** compounds; ellipsoids are displayed at the 50% probability level.