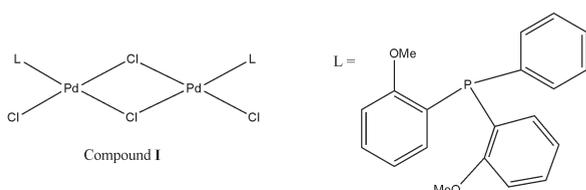


agents [2]. However, the information on the regioselectivity of the corresponding reaction of simple α -olefins is fragmentary, particularly with regard to branched chain selectivity.

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.



- [1] L. Kollár, *Modern Carbonylation Methods* **2008**, Wiley-VCH, Weinheim. [2] J. Tsuji, *Palladium Reagents and Catalysis* **1997**, Wiley, Chichester. [3] F.P. Chiusoli, P.M. Maitlis, *Metal-catalysis in Industrial Organic Processes* RSC Publications, Cambridge. **2006**. [4] D.B.G. Williams, M.L. Shaw, M.L. Green, C.W. Holzappel, *Angew. Chem. Int. Ed.* **2008**, *47*, 560. [5] R.P. Tooze, K. Whistn, A.P. Malyan, M.J. Taylor, N. Wilson, *Dalton Trans.* **2000**, 3441. [6] C. van Blerk, C.W. Holzappel, *Acta. Cryst.* **2009**, *E65*, m1341. [7] C. van Blerk, C.W. Holzappel, *Acta. Cryst.* **2009**, *E65*, m1342. [8] C. van Blerk, C.W. Holzappel, *Acta. Cryst.* **2009**, *E65*, m1536. [9] C. Arderne, C.W. Holzappel, *Acta. Cryst.* **2011**, *E67*, in preparation.

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

MS31.P21

Acta Cryst. (2011) **A67**, C432

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 $[\text{Ln}_2(\text{C}_2\text{H}_4\text{C}_2\text{O}_4)_2(\text{SO}_4)(\text{H}_2\text{O})_2]$ [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 ($\mu_4 \eta^2$) 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 comparison with analogues hydrates, as may be seen in the thermal analysis.

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

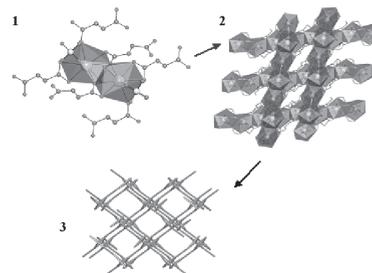


Fig 1. Building block of the isostructural compounds (1) and tridimensional representations (2, 3).

- [1] M.C. Bernini, E.V. Brusau, G.E. Narda, G.E. Echeverria, C.G. Pozzi, G.Punte, C.W. Lehmann, *Eur. J. Inorg. Chem.* **2007**, 684–693. H-T. Zhang, Y. Song, Y-X. Li, J-L. Zuo, S. Gao, and X-Z. You, *Eur. J. Inorg. Chem.* **2005**, 766–772. S.C. Manna, E. Zangrando, A. Bencini, C. Benelli, N.R. Chaudhuri, *Inorg. Chem.* **2006**, *45*, 9114-9122.

Keywords: lanthanide MOFs, Sulfate-succinate, Heterogeneous catalysis

MS31.P22

Acta Cryst. (2011) **A67**, C432-C433

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 $[\text{Zn}_3(\text{H}_2\text{O})(\text{C}_{19}\text{O}_8\text{H}_7\text{F}_6)](\text{H}_2\text{O})_{0.33}$ (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 Schläfli symbol: $\{8^3\}$, vertex symbol with circuits: $[8.8.8(2)]$. Topological classification was done with TOPOS¹ and optimized with SYSTRE².

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].

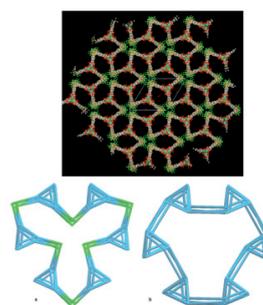


Figure 1 up: Crystal Structure of $[\text{Zn}_3(\text{H}_2\text{O})(\text{C}_{19}\text{O}_8\text{H}_7\text{F}_6)](\text{H}_2\text{O})_{0.33}$, **down:** topology of decorated net (a), not decorated net (b).