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We report here the *ab initio* crystal structure solution of three $MgCl_2 \cdot nC_2H_5OH$ adducts, precisely $2MgCl_2 \cdot 3EtOH$ ($n=1.5$), $5MgCl_2 \cdot 14EtOH$ ($n=2.8$) and $3MgCl_2 \cdot 10EtOH$ ($n=3.3$), obtained from high-resolution X-ray powder diffraction data collected using synchrotron radiation (ID31 at ESRF, Grenoble).

The above-mentioned complexes are fundamental precursors of the latest generation Ziegler-Natta catalysts, which consist of $TiCl_4$ supported on $MgCl_2$, used to produce polyolefins on a global scale. The catalytic yield and isotacticity degree of the derived polymers strongly depend on the Lewis base-to- $MgCl_2$ ratio of the $MgCl_2 \cdot nEtOH$ adducts [1]. It has been suggested that the formation of $MgCl_2/TiCl_4$, produced with $MgCl_2$ /Lewis base complexes, retains the memory of the ligand distribution in the precursor [2]. The catalyst models developed to date are based on the insertion of $TiCl_4$ species and donors on selected cut surfaces of α - $MgCl_2$ [3]; whereas the effects of the precursor properties on the catalytic activity are invariably neglected due to the lack of knowledge of the precursor atomic structures.

Our direct structural analysis confirmed that the structures of $MgCl_2 \cdot nEtOH$ adducts with $n=1.5$ and $n=2.8$ are based on ribbons of metal-centered octahedra similar to $MnCl_2 \cdot nEtOH$ complexes, as previously suggested [4, 2]. However the bonding scheme in $MgCl_2 \cdot nEtOH$ with $n=1.5$ is different when compared to the $MnCl_2 \cdot nEtOH$ complex with the same stoichiometry. With $n=3.3$ the chain-like structure of the $MgCl_2 \cdot nEtOH$ complex breaks in a thread-like structure of isolated octahedra linked by hydrogen bonds. The different bonding network and packing model of the chain-like and thread-like isomers will be the starting point to model the formation of different condensed blocks upon de-alcoholation.

Therefore, we predict that the structural description at atomic scale of $MgCl_2 \cdot nEtOH$ supports will offer new possibilities to model and to improve the performances of Ziegler-Natta catalysts at the industrial level.

[1] R. Huang, F. Malizia, G. Pennini, C.E. Koning, J.C. Chadwick, *Macromol. Rapid Commun.* **2008**, *29*, 1732-1738. [2] P. Sozzani, S. Bracco, A. Comotti, R. Simonutti, I. Camurati, *J. Am. Chem. Soc.* **2003**, *125*, 12881-12893. [3] K. Vanka, G. Singh, D. Iyer, V. Gupta, *J. Phys. Chem. C* **2010**, *114*, 15771-15781. [4] a) P.L'Haridon, M.T. LeBihan, Y. Laurent, *Acta Cryst.* **1972**, *B28*, 2743-2748, b) P.L'Haridon, M.T. LeBihan, *Acta Cryst.* **1973**, *B29*, 2195-2203.

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Influence of a robust supramolecular synthon on structure-property relationships in ammonium carboxylates

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One of the aims of crystal engineering is to produce crystalline materials with predictable and reproducible supramolecular interactions. Although a number of other interactions are possible, the most common supramolecular "glue" used in crystal engineering is the hydrogen bond.

We have recently undertaken a systematic survey of the charge-assisted supramolecular heterosynths that occur in ammonium carboxylate salts [1-4]. Most structures reported previously incorporate

either regularly repeating hydrogen-bonded rings propagated by a 2-fold screw axis or alternating hydrogen bonded rings propagated by a centre of inversion. We set out to examine how robust these supramolecular synths would be under the influence of various molecular interferences. Compounds have been characterised by single crystal and powder X-ray diffraction. Their thermal stability and decomposition behaviour have been studied using Differential Scanning Calorimetry, Thermogravimetry and Hot Stage Microscopy.

Active pharmaceutical ingredients (API) suffer from some disadvantages in the solid state, particularly poor solubility or bioavailability and polymorphism. By making use of crystal engineering concepts to make pharmaceutical co-crystals and pharmaceutical salts, which are hydrogen bonded assemblies between the API and a GRAS (generally-regarded-as-safe) substance, it is possible to increase the water solubility, or to reduce the likelihood of polymorphic behaviour of the API itself. The same supramolecular synths are observed in amine salts of carboxylic acid containing APIs such as (S)-Ibuprofen, Diclofenac and Fenofibrate [5]. We have found that these supramolecular synths are extremely robust but can be switched off under the influence of various molecular interferences. We have also established some principles involving the physical properties (such as melting points and solubilities) of materials containing these supramolecular synths.

[1] A. Lemmerer, S.A. Bourne, M.A. Fernandes. *Crystal Growth & Design*, **2008**, *8*, 1106-1109. [2] A. Lemmerer, S.A. Bourne, M.A. Fernandes. *CrystEngComm*. **2008**, *10*, 1605-1612. [3] A. Lemmerer, S.A. Bourne, M.A. Fernandes. *CrystEngComm*, **2008**, *10*, 1750-1757. [4] A. Lemmerer, N.B. Báthori, S.A. Bourne. *Acta Cryst.* **2008**, *B64*, 780-790. [5] A. Lemmerer, S.A. Bourne, M.R. Caira, J. Cotton, U. Hendricks, L.C. Peinke, L. Trollope. *CrystEngComm*, **2010**, *12*, 3634-3641.

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Predictive approach of new bismuth oxo-phosphates

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One important challenge in today's solid state chemistry is to be able to conceive materials with particular physico-chemical properties. The possibility of predicting new structures according to a wished property and the faculty to formulate it, is surely a main advantage in the design of new materials.

In the Bi_2O_3 - M_xO_y - P_2O_5 ternary systems, on the basis of previous compounds based on 2D-ribbon like units [1] [2], we have prepared numerous compounds with an original predictive approach, based

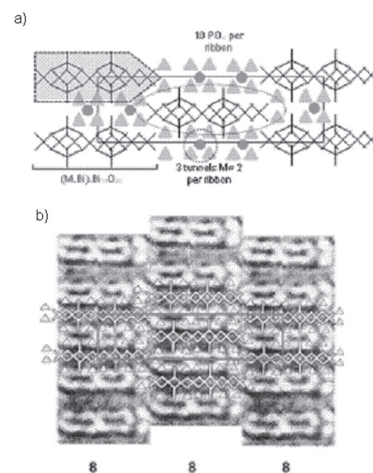


Figure 1: a) Design of a predicted structure $n=8$, b) HREM image showing the evidence of a new intergrowth (Structural verification).