EUROPEAN SYNCHROTRON RADIATION FACILITY
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Experiment Report Form

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ESRF	**Experiment title:** Crystal structure determination of microporous $MgCl_2$ *n*EtOH complexes used as supports for Ziegler-Natta catalysts	**Experiment number**: CH-2924
Beamline: ID31	**Date of experiment**: from: 27/09/2009 to: 29/09/2009	**Date of report**:
Shifts: 6	**Local contact(s)**: Dr. Adrian Hill	*Received at ESRF:*

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Report:

The aim of the CH-2924 experiment was the determination of the crystal structure of $MgCl_2$-Ethanol complexes. The importance of this goal lies in the fact that the studied $MgCl_2$-Ethanol complexes are the building blocks of Ziegler-Natta catalyst supports used in the production of polyolefins, such as polyethylene and polypropylene on a multi-million ton scale world-wide. Knowledge of their structure, at the atomic level, will facilitate better comprehension of the Ziegler-Natta catalysis. This is principally because the catalyst models developed up until now completely neglect the link to the structure of the $MgCl_2$ precursor: they are only based on the insertion of $TiCl_4$ species and donors on selected cut surfaces of α-$MgCl_2$. The structural elucidation of the $MgCl_2$·nEtOH complexes has been a long-standing problem and numerous attempts have failed in the past for the difficulties in obtaining pure phases of stable forms and because the *ab initio* structure solution from powder diffraction patterns remains a challenging task, especially for low symmetry compounds (triclinic, in our case), which requires high resolution data.
Our synchrotron measurements were performed on three $MgCl_2$·*n*EtOH (n=1.5, 2.8 and 3.3) complexes prepared according to synthesis route devised at the Giulio Natta Research and Development Centre (LyondellBasell, Ferrara, Italy). The composition of all the complexes was checked for ethanol content by using GC-FID (Flame Ionisation Detector) technique and by elemental analysis for magnesium and chlorine determination. Due to the hydrophilic nature of these compounds, where ethanol is readily replaced by water molecules, the synthesized samples were immediately transferred and kept in a dry chamber. Several borosilicate glass capillaries were then filled with each of the three compounds and hermetically sealed by

welding the open tip. Laboratory powder diffraction patterns were collected on these capillaries at different times after preparation in order to check for sample purity and possible transformation.
The high-resolution synchrotron X-ray powder diffraction patterns were collected at the beam line ID31. The beam line was set to deliver a wavelength of 0.5 Å which was calibrated by a silicon standard. Placed in borosilicate capillaries of 1.0 mm in diameter, the samples were spun and translated during data collection in order to minimize preferred orientation and radiation damage, respectively. Data were collected at room temperature, in continuous mode across a range of $1 \leq 2\Theta \leq 65°$, with accumulation times increasing with the scattering angle, and rebinned with a step size of 0.002° 2Θ.
Indexing of the synchrotron powder diffraction patterns and space-group determination of $MgCl_2 \cdot n$EtOH (n = 1.5, 2.8, 3.3) were successfully achieved by the Crysfire suite of programs, in particular using ITO. A subsequent cell-constrained profile fitting conducted by the Le Bail method was performed using the GSAS-EXPGUI package. The *ab initio* crystal structure solution was carried out by a combination of direct methods and the simulated annealing approach using the EXPO2009 program. The previously determined space group and refined unit cell parameters, along with the chemical content of the unit cell were entered as previous information. In the case of $MgCl_2 \cdot 1.5$EtOH the powder pattern was subtracted by the contribution of two hydrated magnesium chloride phases before the structure solution step. In all three cases EXPO2009 provided structural models that included the positions of magnesium, chlorine, oxygen and carbon atoms. These starting models were then refined by GSAS-EXPGUI. The position of the ethanol molecules (including the hydrogen atoms not located during structure solution and refinement) were obtained by a modelling and optimization procedure using the Moldraw program.
The obtained crystal structure models for $2MgCl_2 \cdot 3$EtOH (n=1.5), $5MgCl_2 \cdot 14$EtOH (n=2.8) and $3MgCl_2 \cdot 10$EtOH (n=3.3) have been deposited in the ICSD and CSD crystallographic databases and a manuscript entitled "The crystal structure of Ziegler-Natta catalyst supports", by Malizia, Cruciani and Fait, has been submitted to the *Angewandte Chemie International Edition* journal (we are waiting for the Editor's decision). The following Figures show the final Rietveld fit obtained for the three $MgCl_2 \cdot n$EtOH complexes.

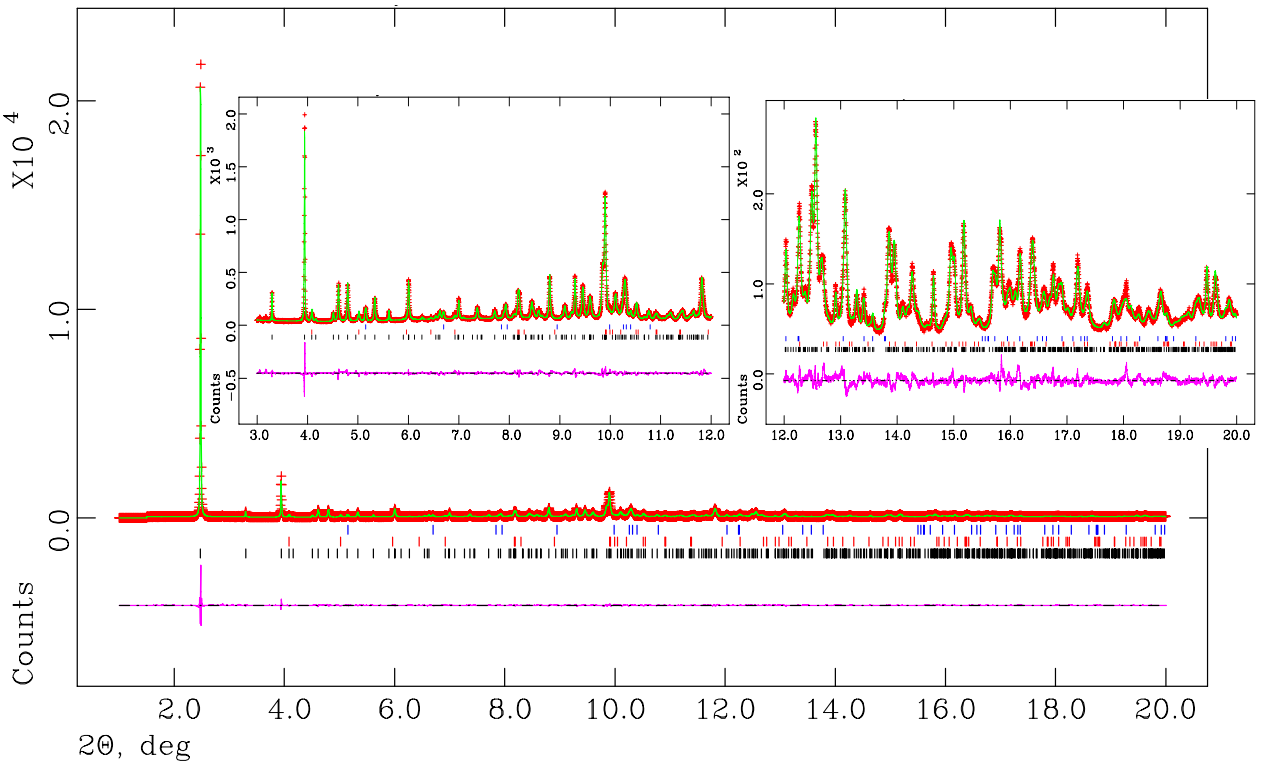

Figure 1. Final Rietveld fit for the $MgCl_2 \cdot 1.5$EtOH sample. Intermediate and high angle 2θ regions are also plotted in the expanded intensity scale. Marks refer to Bragg peak positions of phases included in refinement - from the bottom, with relevant weight fractions: a) $MgCl_2 \cdot 1.5$EtOH, 92(1) wt %; b) $MgCl_2 \cdot 2H_2O$, 5(1) wt % and c) $MgCl_2 \cdot 1H_2O$, 3(1) wt %.

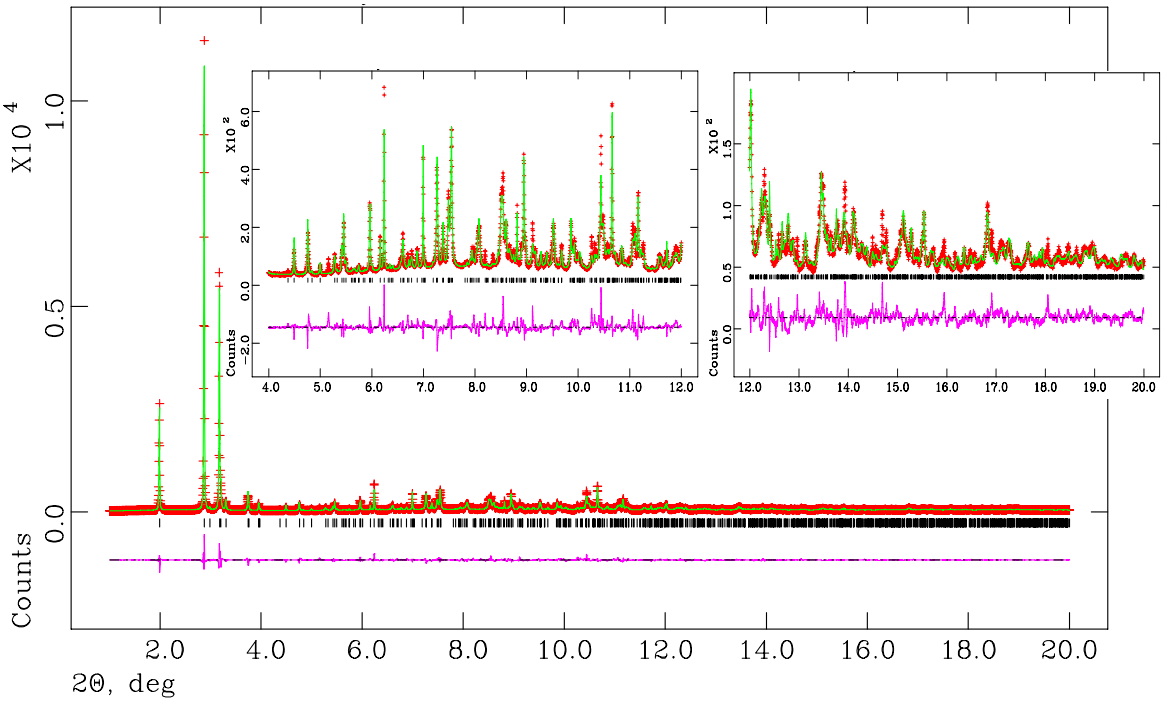

Figure 2. Final Rietveld fit for the $MgCl_2 \cdot 2.8EtOH$ sample. Intermediate and high angle 2θ regions are also plotted in the expanded intensity scale. Marks refer to Bragg peak positions of phase included in refinement: $MgCl_2 \cdot 2.8EtOH$.

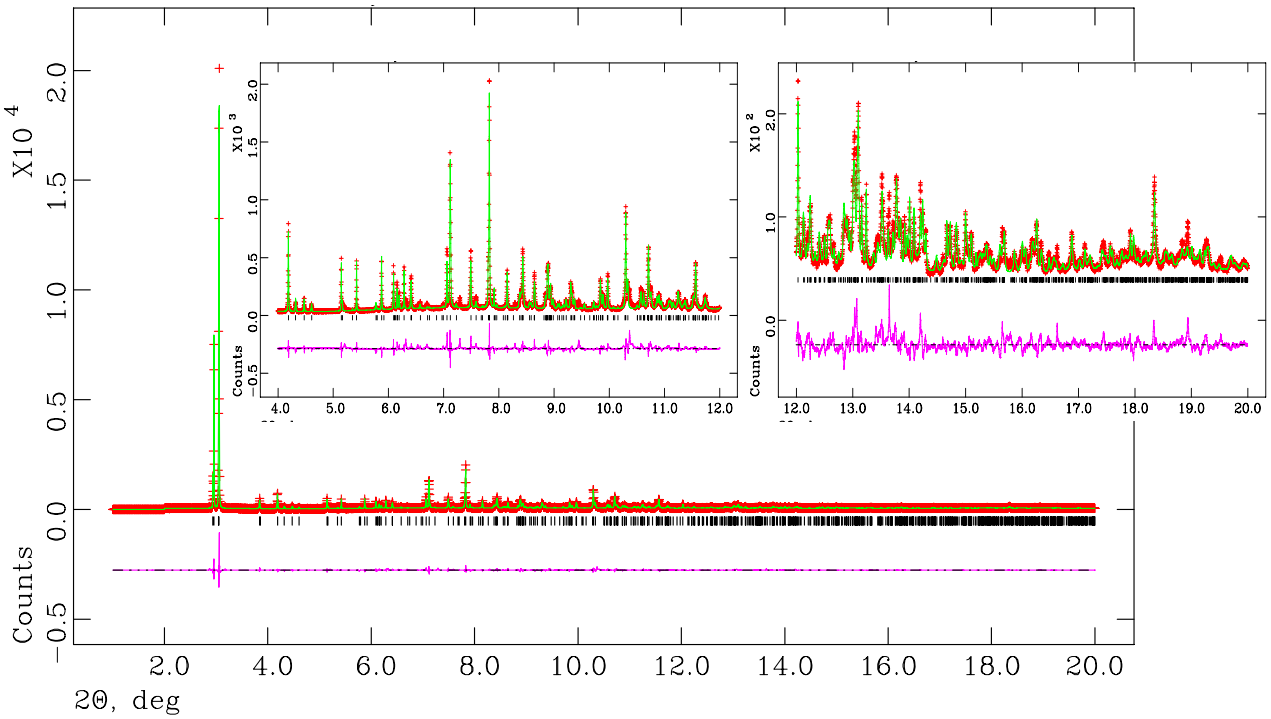

Figure 3. Final Rietveld fit for the $MgCl_2 \cdot 3.3EtOH$ sample. Intermediate and high angle 2θ regions are also plotted in the expanded intensity scale. Marks refer to Bragg peak positions of phase included in refinement: $MgCl_2 \cdot 3.3EtOH$.