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Keywords: copper complex, topology, hydrothermal synthesis

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Influence of the Substituent in the Crystal Packing of Copper(II)-malonates

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The design of new molecular materials with interesting magnetic properties can be achieved following different approaches. The introduction of a secondary ligand, the combination of metal centres or the modification of the primary ligand can be some of these strategies. In the context of our magneto-structural research with malonato-bridged copper(II) complexes and in order to obtain novel coordination modes that could enhance the magnetic exchange coupling we have studied the influence of the substituted malonate ligand in copper(II) complexes.

Complexes of the form $[\text{Cu}(\text{L}^{\text{I}})(\text{H}_2\text{O})_n]$ and $[\text{Cu}(\text{L}^{\text{II}})_2(\text{H}_2\text{O})_n]$ $[\text{Cu}(\text{H}_2\text{O})_n]$ with L^{I} = malonate, ethylmalonate, methylmalonate and L^{II} = malonate, phenylmalonate, are synthesized. Crystal structures vary from the discrete units of copper(II) malonate compounds [1] to the different conformations of two-dimensional structures of ethylmalonate and methylmalonate. Overall ferromagnetic exchange coupling is found in all of these compounds.

Subtle changes in the nature of the substituent can modify the crystal packing and hence the magnetic properties present in these compounds.

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Keywords: copper coordination compounds, crystal packing, magnetic properties

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Hydrogen Storage in Metal-Organic Frameworks

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Reticular synthesis (logical construction of networks from molecular building blocks) has yielded a new class of crystalline porous materials commonly referred to as metal-organic frameworks (MOFs) in which metal ions and clusters are linked by organic units. The ability to prepare MOFs in high yield and with adjustable pore size, shape and functionality has led to their study as gas sorption materials. We have demonstrated that systematic variation of the organic component in isoreticular metal-organic frameworks (IRMOFs) has a marked effect on their capacities for methane. More recently, we discovered that IRMOFs are also capable of storing significant amounts of H_2 , and inelastic neutron scattering studies of molecular hydrogen adsorbed in IRMOF-1 pointed to the organic unit as one of the important adsorption sites. Thus, there is an acute need to collect and analyze more hydrogen uptake measurements on such materials in order to establish the favorable factors for its storage. Hydrogen adsorption isotherms measured at 77 K show a distinct dependence of uptake on the nature of the link for a set of five MOF materials containing the $\text{Zn}_4\text{O}(\text{CO}_2)_6$ cluster. At 1 atm, the materials sorb between 4.2 and 9.3 molecules of H_2 per formula unit. The results imply a trend in hydrogen capacity with the number of rings in the organic moiety. Additionally, the significant influence of the inorganic unit, namely when open metal sites are present, on hydrogen uptake will be presented.

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Keywords: hydrogen storage, metal-organic frameworks, adsorption

MS53 MATERIALS FOR ENERGY CONVERSION AND STORAGE

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Electrochemical Materials – Structure in Action

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There are a number of different examples of how *in situ* X-ray diffraction have been used to study lithium insertion/extraction mechanisms of electrode materials in Li-ion batteries [1,2]. In general, the structural changes during a continuous discharge or charge of the battery are followed, giving information about phase transformations in the material. Few, however, have utilized *in situ* X-ray diffraction during potential steps to get time resolved information of the material's response to, for instance, pulsed charges. With the use of synchrotron radiation with high beam intensity and therefore fast exposure times, new results will be presented for some important cathode materials in Li-ion batteries, for example $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, vanadium-oxide nanotubes and Mo_6S_8 . For this purpose, different instrument geometries and detector systems for transmission mode have been explored in combination with special built sample holders. All the experiments have been carried out at MAXlab, the Swedish synchrotron radiation source but the quality of the result will be discussed in the light of earlier obtained results using "in-house" *in situ* X-ray diffraction.

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Keywords: battery materials, time-resolved scattering studies, synchrotron X-ray diffraction

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PDF and NMR Study of Ordering in the Positive Electrode Material $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$

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The local environments and short-range ordering of $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$, a potential Li-ion battery positive electrode material^{1,2}, were investigated by using a combination of X-ray and neutron diffraction and isotopic substitution, Li MAS NMR spectroscopy and, for the first time, X-ray and neutron Pair Distribution Function (PDF) analysis, associated with Reverse Monte Carlo (RMC) calculations. $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$ adopts the LiCoO_2 structure and comprises separate Li layers, transition metal (Ni,Mn) layers and O layers.

NMR experiments and Rietveld refinements showed that there is 10% of Li/Ni site exchange. Neutron PDF analysis revealed considerable local distortions in the layers that are not captured in the LiCoO_2 model. Large clusters were built to investigate cation ordering, by performing RMC calculations. Both NMR and RMC were consistent with a non-random distribution of Ni, Mn and Li cations in the transition metal layers. Constraints from both methods showed the presence of short-range order in the transition metal layers comprising LiMn_6 and LiMn_5Ni clusters combined with Ni and Mn contacts that are consistent with those found in some of the proposed structures based on Li_2MnO_3 -like ordering of the cations.

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Keywords: lithium batteries, pair distribution function, NMR