

P08.15.178*Acta Cryst.* (2008). A64, C473**Structural studies and thermal decomposition of light complex hydride**

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One of the greatest technological barriers of widespread introduction of hydrogen in global energy systems is an efficient and safe storage method. Hydrogen chemically bonded in metals or intermetallic alloys constitutes a storage alternative where very high volumetric densities can be obtained. However, in the known materials for hydrogen storage, it is always a trade-off between volumetric densities, gravimetric densities, stability, kinetics, price and safety. During the last years new hydrogen storage materials with improved properties have been synthesized and characterized. In particular novel complex hydrides based on the elements aluminium, boron, magnesium and nitrogen have been extensively studied. Alane, AlH_3 , is of interest because of its very high volumetric and gravimetric hydrogen density and low decomposition temperature. 3 polymorphs (alpha prime, beta and gamma) with previously unknown crystal structures have been characterized with combined high-resolution synchrotron radiation powder diffraction (SR-PXD) and neutron powder diffraction (NPD). Their thermal decomposition behaviours were investigated by *in-situ* SR-PXD, revealing an intermingling of phase transitions and decomposition. *In-situ* SR-PXD combined with Raman spectroscopy was used to investigate thermal decomposition of $\text{Ca}(\text{BH}_4)_2$. The decomposition route involves several phase transitions and intermediate phases in both crystalline and amorphous state. Li_2NH is an important phase in M-Li-N-H systems but the crystal structure has been debated. NPD and SR-PXD data collected from a double isotope substituted sample, $^7\text{LiND}_2$, clearly show that the unit cell is larger and the symmetry is lower than the previously suggested.

Keywords: synchrotron powder diffraction, neutron powder diffraction, hydrogen storage

P08.14.179*Acta Cryst.* (2008). A64, C473**Structures of Li_2MnO_3 for lithium battery electrode materials**

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Lithium manganese oxide, Li_2MnO_3 , is proposed for cathode materials of high-energy density for lithium secondary batteries. Li_2MnO_3 has a rock-salt type structure with alternating Li layers and Li-Mn layers separated by closed-packed oxygen arrays. The disordered arrangements in the each layers along c-axis varied with the heat treatment temperature and the disordering affects its electrochemical property. In this study, the structure of Li_2MnO_3 was studied by X-ray diffraction measurement and DIFFaX simulation for considering stacking fault in the structure. The relationship between the structures and electrochemical properties was studied. Fig. 1 shows a model of stacking fault for the Li-Mn layer used for DIFFaX simulation. The stacking of SV1 corresponds to the original

structure described by space group $C2/m$. In the SV2 and 2' stacking, Li exists in the Mn position by a translation of Li-Mn layer where Li and Mn exchanged. The samples heated at 600 and 800 °C were mainly composed of a random combination of SV1, 2 and 2', and the structure of the SV1', 3 and 3' was less than 10%. The electrochemical properties are discussed based on the stacking sequence.

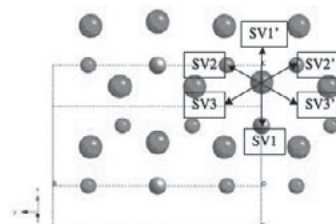


Fig.1 Stacking fault model of Li-Mn layer.

Keywords: lithium battery, stacking fault, electrode

P08.14.180*Acta Cryst.* (2008). A64, C473**Studies of the nanostructure of natural vegetable fibers**

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Vegetable fiber is a wonder of the nature, a most important and widespread natural organic polymer. The chemical structure of the native cellulose, a basic component of the natural vegetable fiber, as a linear β -1,4-Glucose chain is well accepted. However, the physical structure creating the wonderful network of the supermolecular order of this fiber is not yet completely clear. From our experiments with ESR, especially with the called "ESR Spectroscopy - Tomography", in combination with other methods (X-ray diffraction, SEM, AFM, Polarized Light) on different genera of vegetable fibers (such as cotton, jute, pineapple, sisal, bamboo), we have to the first time discovered that the inside structure of the vegetable fiber is constituted not only by polysaccharide cellulose, but also by another very important component consists of fivefold [2Fe-2S] super-exchange metallo-organic combinations. These persist in the form of the composite aperiodic Nanostructures linking diagonally the cellulose chains creating an elementary fiber. A visible "macroscopic practical fiber" is constituted by a lot of the elementary fibers spiraling together about an axis by a sloping angle $\theta = 54.7^\circ$. This spiral angle is of a deep significance on the statistic quantum electron dynamics and the biophysical function of the fibers in the nature. This fivefold metallo-organic composite Nanostructure plays a decisive role in the specific features of vegetable fibers (such as the strength, the torsional module, the conductivity, the radiation response). On the basis of these achieved results, some physical and biological treatment techniques to improve fiber properties have been examined.

Keywords: nanostructure of natural vegetable fibers, organometallic composite nanostructure of vegetable fibers, fivefold organometallic nanostructure of vegetable fibers

P08.10.181*Acta Cryst.* (2008). A64, C473-474**Concomitant polymorphism and twinning of dichloro-bis(η -5-tert-butylcyclopentadienyl)titanium(IV)**

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The title compound (I) crystallizes in the orthorhombic space group $P2_12_12$ ($a=10.7028 \text{ \AA}$, $b=12.8508 \text{ \AA}$, $c=6.5844 \text{ \AA}$, $V=905.62 \text{ \AA}^3$) at 298 K (phase I). The Ti complex resides on a two-fold axis with $Z'=0.5$. Complex (I) undergoes two sharp enantiotropic phase transitions upon cooling. The first transformation occurs at 293 K to yield a unit cell with a doubled c axis ($a=10.5539 \text{ \AA}$, $b=12.8757 \text{ \AA}$, $c=13.0817 \text{ \AA}$, $V=1777.66 \text{ \AA}^3$) at 175 K) and the orthorhombic space group $P2_12_12_1$ (phase II). The doubling of the unit cell volume results in the addition of a translational component to the two-fold rotational symmetry in the c direction, and now the complex is in a general position. The second transition takes place at 147 K to convert the single crystal into a merohedrally twinned crystal with two monoclinic components of half the size ($a=10.5529 \text{ \AA}$, $b=12.7403 \text{ \AA}$, $c=6.5486 \text{ \AA}$, $\beta=92.327^\circ$, $V=879.71 \text{ \AA}^3$) at 100 K) in the monoclinic space group $P2_1$ (phase III). The Ti complex remains in a general position. The concomitant phase transition and twinning necessarily result in the loss of symmetry along the a and c axes and can be thought of as taking the b axis in phase II and "pulling" (shifting) it in the positive direction to generate the twinning in phase III (see diagram). The unique angle widens as the temperature is lowered. The variable temperature study of the selected crystal was conducted in an automated mode on a Bruker SMART APEX2 diffractometer with Cu $K\alpha$ radiation while the exact transition temperatures were manually pinpointed with Mo $K\alpha$ radiation. The molecular symmetry evaluations and exact refinement procedures are also discussed.

Keywords: Polymorphism, Twinning, Solid phase transitions

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Knowledge-based design of host-guest interactions in wheel-and-axle inorganic diols

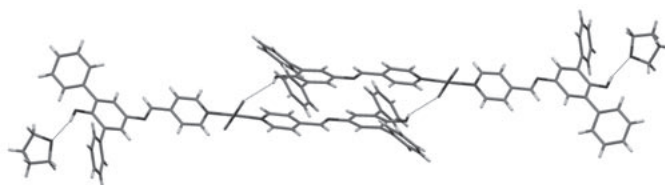
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We are interested in the design of hybrid organic-inorganic wheel-and-axle systems (waad) with flexible dynamic frameworks that can create pores "on demand" to accommodate small guest molecules [1-3]. A reversible dynamic reorganization between the waad non-solvate and solvate phases requires two conditions: (i) a low cost structural rearrangement between two states represented by the initial close (self-mediated) and the final open (guest-mediated) host frameworks, (ii) an easily accessible migration path for the outgoing and incoming guest molecules. Palladium complexes of triarylcarbinol ligands have shown suitable structural requisites to give reversible host-guest properties [2, 3]. New iminic ligands designed on this basis result very promising promoters of potentially bistable supramolecular architectures based on metallo-organic supramolecular building units as wide as 40 Å (Figure).

References

- [1] M.R. Caira, A. Jacobs, L.R. Nassimbeni, F. Toda, *CrystEngComm*, 2003, 5, 150
- [2] A. Bacchi, E. Bosetti, M. Carcelli, *CrystEngComm*, 2005, 7, 527-537
- [3] A. Bacchi, E. Bosetti, M. Carcelli, P. Pelagatti, D. Rogolino, G. Pelizzi, *Inorganic Chemistry*, 2005, 44, 431-442



Keywords: host-guest complexes, supramolecular assemblies, crystal engineering

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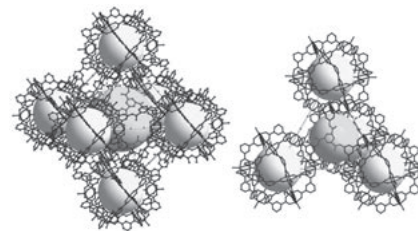
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A designed metal-organic framework based on a metal-organic polyhedron

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Metal-organic frameworks (MOFs) based on metal-organic polyhedra (MOPs) might provide efficient ways for the construction of designed porous MOFs, because MOPs themselves have their inherent cavities. We have prepared a (3,24)-connected MOF, $[Zn_{24}(L)_8(H_2O)_{24}]_n$, using a C_3 symmetric tritopic ligand, 5,5',5''-[1,3,5-benzenetriyltris(carbonylimino)]tris-1,3-benzenedicarboxylic acid (H6L). The carboxylate groups of 1,3-benzenedicarboxylate unit of the ligand can be combined with Zn^{2+} ion to form paddle wheel secondary building units, $Zn_2(COO)_4$, which produce an edge-directed corner-linked metal-organic cuboctahedron (MOC). The planar C_3 symmetric tritopic character of the ligand can force all of the resulting MOCs to a triangular arrangement for a cubic close packing (CCP) arrangement at all 24 edges of the cuboctahedron. This CCP arrangement of the MOCs led to additional superoctahedral and supertetrahedral cavities. Though the (3,24)-connected MOF represents the highest connected network topology presently known for frameworks corresponds to ~71% of the total crystal volume.



Keywords: metal-organic framework, metal-organic polyhedra, metal-organic cuboctahedron

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Properties of metal-organometallic frameworks derived from facially η^6 metalated terephthalates

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Interest in the design and synthesis of metal-organometallic