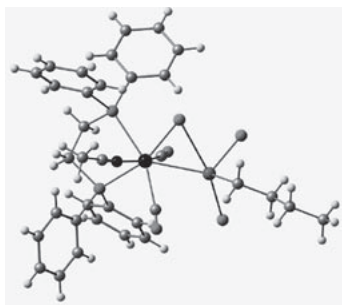


[Mo(CO)₃(NCMe)₂(SnBuCl₂)Cl], **1**, reacted with phosphanes (Ph₂PCH₂CH₂PPh₂, dppe; Ph₂PCH₂PPh₂, dppm; Ph₂PNHPPPh₂, dppa) to afford complexes [Mo(CO)₂(NCMe)(P-P)(SnBuCl₂)Cl] (L=dppe **2**, dppm **3**, dppa **4**). When these complexes reacted with [NH₄][S₂P(OEt)₂], the nitrile and the chloride ligands were replaced by the S₂P(OEt)₂ anionic ligand, yielding [Mo(CO)₂(S₂P(OEt)₂)(P-P)(SnBuCl₂)] (L=dppe **5**, dppm **6**, dppa **7**). Complexes **5**, **6**, and **7** could also be obtained from a 'one pot' reaction starting from Mo(CO)₆, SnBuCl₃, [NH₄][S₂P(OEt)₂] and the appropriate phosphane. Similar reactions took place when SnPhCl₂ was used instead of SnBuCl₂ in the starting material, leading to the three complexes [Mo(CO)₂(S₂P(OEt)₂)(P-P)(SnPhCl₂)] (L=dppe **8**, dppm **9**, dppa **10**). The structure of complexes **2**, **3**, **5**, **6**, **8**, **9**, **10** were determined using single crystal X-ray diffraction. In these complexes, Mo(II) is heptacoordinate, with a Mo-Sn bond. The tin atom has a tetrahedral environment in all the complexes, except in [Mo(CO)₂(NCMe)(dppe)(SnBuCl₂)Cl] (**2**, figure), where the Cl ligand bridges Mo and Sn. DFT (Density Functional Theory) calculations were performed in order to discuss the nature of the Mo-Sn bond.



Keywords: Mo(II) complexes, Sn derivatives, crystal structures

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Guest-dependent high-pressure behavior in a nanoporous metal-organic framework material

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The structural and chemical versatility of metal-organic framework (MOF) materials underlie important technological, industrial, and environmental applications, including in strategic gas storage and separation. The extensive structural complexities now well-documented for these systems are likely to be associated with unprecedented pressure-induced behavior compared with the traditional solid state materials more commonly explored under high pressure conditions. Furthermore, the typically open (low density, often porous) nature of MOF materials is likely to induce such phenomena at more moderated pressures, such as may be routinely encountered in practical applications. For example, densification of powdered nanoporous MOF materials to optimize volumetric gas storage capacity through sample compression (up to several GPa) may distort the framework and pore structure, and accordingly may significantly alter the guest sorption properties (e.g., selectivity). Accordingly, understanding the impact of pressure on MOF systems is not only of considerable fundamental interest, but is relevant to the applications for which MOF materials are being considered. Here we report the structural investigation of a nanoporous MOF material at high pressures within a diamond anvil cell using synchrotron-based X-ray powder diffraction.

Keywords: high-pressure X-ray diffraction, microporous materials, coordination polymers

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Femtosecond to hours structural dynamics of self-assembling systems

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In the following we will present time-resolved small angle x-ray scattering studies on photoactive, self-organising systems like photo-sensitized liquid crystal systems and other reference systems of biological relevance. In the first system, we have studied the kinetics and dynamics of the photo-induced phase transition from a liquid crystal to a microemulsion system and vice versa. In the second system, we mainly concentrate on the structural response function upon photo-irradiation. In the millisecond time domain, the structural dynamics studies have been performed at home-based time-resolved photo small angle X-ray diffraction apparatus [1, 2], the nanosecond and picosecond time scale have been explored employing plasma based home laboratory sources and synchrotron based x-ray scattering sources (ID09B beamline / ESRF, France) [3] and the femtosecond time domain has been investigated employing the FLASH free electron laser facility at DESY, Germany. We will give an overview over the varying time-scales underlying the photo-activated structural transformation processes. We will also discuss the various x-ray sources and compare the different experimental approaches.

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[2] W. Quevedo, M. Petri, G. Busse, S. Techert, J. Chem. Phys., in press (2008).

[3] submitted.

Keywords: time-resolved x-ray scattering, ultrafast processes, structural dynamics

P08.13.80

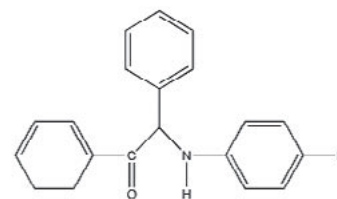
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Dimers or not dimers in 1-arylanilinoethanones

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Few 1-arylaminoethanone derivatives have been structurally characterised up to date. However, these derivatives are important in synthesis and some of them possess interesting charge-transfer properties while also displaying rather unusual supramolecular arrangements. In the present study we present results from our structural characterisation of four derivatives, with substitutions (Cl-, MeO-, H-, Me-) in the 4-anilino position of the 1-arylaminoethanones. The Cl- and Me- derivatives form distant dimers while MeO- and H- derivatives are found as monomers. The formation of distant dimers has been found to be related to the planarity of the N atom in these structures, in agreement with the formation of similar dimers



R = Cl, MeO, H, Me

in the Br- and NO₂- derivatives of 1-phenylethanones (1,2). However, when the N atom in these structures is pyramidal, no distant dimers are formed and the N-H...C(aryl) contacts become evident.

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Keywords: hydrogen bonds in organic crystals, small molecules organic, long-range contacts

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The interaction between H-bond and polyhedral network in the polymorphs of aluminium hydroxide

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We have investigated several polymorphs of aluminium hydroxide in the last few years. The most important of these is the structural investigation under pressure of the hydrogen bond (H-bond) in δ -AlOOH, a phase which is a potential water reservoir in cold subducted slabs, transporting water into the lower mantle. Structures of aluminium hydroxides could be characterized as a combination of 0D (D: dimensional) or 1D H-bonding network and 2D or 3D dimensional Al(O, OH)₆ polyhedral network. For example, δ -AlOOH is considered to be a combination of 0D H-bond and 3D polyhedral networks. The H-bond and polyhedral networks are not isolated, but interacted each other via valence sum of the oxygen atoms. For example if we consider a fictitious 1D network consists of 0D H-bond and 0D AlO molecule like: -O-Al-O-H_a...O-Al-O-H_b...O-Al-O-H_c..., where H_a is not able to move independently to acceptor site due to the electrostatic valence principle. This can be considered as a kind of 'ice rule.' In this study, we will present the results of x-ray and neutron diffraction studies for δ -AlOOH, β -AlOOH (boehmite), η -Al(OH)₃ and δ -Al(OH)₃. The last two polymorphs are high pressure modifications of γ -Al(OH)₃ (gibbsite), and their structures had remained unknown for quarter of a century after their discovery. η -Al(OH)₃ has the layered structure like gibbsite, and δ -Al(OH)₃ has the A-site deficient perovskite (ReO₃-type) structure. Although the polymorphs of aluminium hydroxide have a large variety of structures, some features of their phase transitions can be understood by the concept that the H-bonding network interacts with the polyhedral network.

Keywords: hydrogen bonding network, high pressure, aluminium hydroxide

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Rationalizing polymorph stability using hydrogen bonding propensities

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Hydrogen bonding is crucial to structural stability in organic crystals, with impact widely reported in the pharmaceutical industry, and elsewhere [1,2]. Here, in an informatics-based approach, the relative stability of polymorphic structures is assessed based on the hydrogen bonding they exhibit. The implicit connection is made between most probable and energetically favourable interactions. The Logit Hydrogen Bonding Propensity method [3] is used to predict preferences for hydrogen bond formation. The method applies data derived from other known compounds to fit a probability model that creates propensity scores for hydrogen bonding atoms to interact in a crystal structure. This flexible method is parameterized to molecular, chemical and crystal structure descriptors. Once a model is derived, target 2D connectivity information at most is required to calculate propensity predictions specific to that target. In this presentation three contrasting drug-like systems will form an application of the method. The examples are modelled using crystal structure datasets from the Cambridge Structural Database (CSD) [4]. The method is also naturally extendable to use of additional e.g. internal company databases. Focus will be paid to statistical relevance and the influence of the model descriptors, which have physically meaningful interpretations. Relevant feedback into the hydrogen bond prediction from those parameters will also be discussed.

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Keywords: polymorphism, cambridge structural database, hydrogen bonding

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The hydrogen bonds in transition-metal oxalate complexes: Influence of Jahn-Teller distortion

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Single crystals of transition-metal oxalate complexes [M(C₂O₄)₂H₂O: M = Mn(II), Fe(II), Co(II), Ni(II)] were synthesized and analyzed by micro-Raman scattering spectroscopy; the O-H stretching bands of the complexes were located at 3324.7 cm⁻¹ for Mn(II), 3305.5 cm⁻¹ for Fe(II), 3324.6 cm⁻¹ for Co(II) and 3340.2 cm⁻¹ for Ni(II), respectively. The stretching wavenumber of O-H decreases considerably with increasing strength (decreasing length) of the hydrogen bond (Libowitzky 1999), and thus the Raman spectra indicated that Fe(II)-oxalate has the strongest hydrogen bonds among the present complexes. The crystal structure of Fe(II)-oxalate was analyzed using single-crystal X-ray diffraction method and refined to the agreement index R1 = 3.22 % calculated for 595 unique observed reflections. This oxalate crystallizes in the monoclinic system, space group C2/c, with unit cell dimensions of a = 12.011(11), b = 5.557(5), c = 9.920(9), β = 128.53(3), V = 518.0(8), and Z = 4. In the crystal structure, the alternation of oxalate anions [(C₂O₄)²⁻] and Fe(II) ions constitute one-dimensional chain structures parallel to [010]; water molecules (H₂O) form hydrogen bonds to link the chains, where