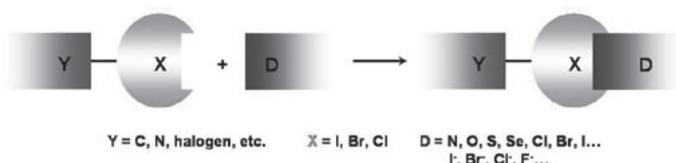


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Halogen atoms are typically located at the periphery of organic molecules and are thus ideally positioned to be involved in intermolecular interactions. Halogen bonding (XB) describes any interaction where halogen atoms function as electrophilic species. XB can be described by the general scheme $D \cdots X-Y$ where X is the electrophilic halogen atom (Lewis acid, XB donor), D is a donor of electron density (Lewis base, XB acceptor), and Y is carbon, nitrogen, halogen, etc. (Scheme 1)[1]. The main features of the interaction will be given and the close similarity with hydrogen bonding will become apparent. Some heuristic principles will be presented in order to develop a rational crystal engineering based on XB. The potential of the interaction will be shown by useful applications in different fields spanning synthetic chemistry, material science, and bioorganic chemistry.

[1] Metrangolo P., Meyer F., Pilati T., Resnati G., Terraneo, G., *Angew. Chem. Int. Ed.* 2008, DOI: 10.1002/anie.200800128 (minireview).



Keywords: halogen bonding, intermolecular interactions, supramolecular chemistry

MS.45.3

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Structural systematic studies of fluoro(pyridinyl) benzamide derivatives

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We are currently studying the crystal structures of a series of Fluoro(pyridinyl)benzamides. Several isomers will be presented including the following:

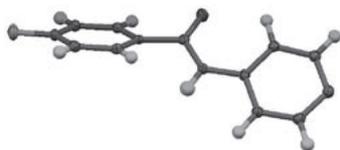
Isomers (I)-(III) $C_{12}H_9FN_2O$, Monoclinic, $P2_1/c$, $Z = 4$, $T = 150K$.

(I) (4-F), $a = 5.6506(3)$, $b = 11.3882(8)$, $c = 15.4314(8)$ Å, $\beta = 95.602(3)^\circ$ $V = 988.27(10)$ Å³, $D_x = 1.453$ Mg.m⁻³, $R = 0.051$.

(II) (3-F), $a = 5.7537(3)$, $b = 11.2421(4)$, $c = 15.1672(7)$ Å, $\beta = 94.188(2)^\circ$ $V = 978.45(8)$ Å³, $D_x = 1.468$ Mg.m⁻³, $R = 0.048$.

(III) (2-F), $a = 5.9832(3)$, $b = 11.1508(5)$, $c = 14.8921(7)$ Å, $\beta = 94.986(3)^\circ$ $V = 989.80(8)$ Å³, $D_x = 1.451$ Mg.m⁻³, $R = 0.044$.

An ORTEP diagram of the molecular structure of (I)



Keywords: isomers, structural systematics, fluorine compounds

MS.45.4

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Crystal engineering using the thiourea moiety

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Crystal engineering¹ is a form of supramolecular synthesis, where discrete molecules use molecular recognition to form supramolecular entities. We aim to identify robust H-bonding synthons that behave predictably in different chemical environments. In studies^{2,3} of a variety of derivatives of monopodal and bipodal acylthioureas with varying side chains R_1 , R_2 and R_3 , we have observed apparently predictable intra- and intermolecular H-bond patterns (Scheme 1) In addition to the H-bonding synthons, these compounds can coordinate to metals through the thiourea moiety. This presentation will consider our own results, together with an analysis of reported structures⁴ to address the following questions:

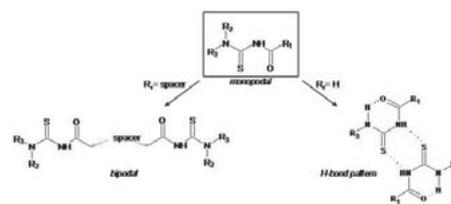
1. How robust is the H-bonding motif for differing R_2 ?
2. Is the same pattern observed in the monopodal and bipodal cases?
3. What is the influence of the R group or the coordinated metal on the H-bonding motif?

1 G. M. J. Schmidt. *Pure Appl. Chem.* 1971, 27, 647.

2 S. A. Bourne, O. Hallale, K. R. Koch, *Crystal Growth & Design*, 2005, 5, 307.

3 O. Hallale, S. A. Bourne, K. R. Koch, *CrystEngComm*, 2005, 7, 161

4 F. H. Allen, *Acta Crystallogr.*, 2002, B58, 380.



Keywords: crystal engineering, hydrogen bonding, thiourea

MS.45.5

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Electrostatic complementarity: A universal theme in molecular crystal structures?

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The nature of protein-protein and protein-ligand interactions has long been discussed on the basis of electrostatic complementarity, where complementary electronegative and electropositive regions are observed to pack adjacent to one-another. Although modern research in crystal engineering, crystal structure prediction and rationalization is overwhelmingly discussed in terms of specific intermolecular interactions, with special reference to the electrostatic properties of molecules, the concept of electrostatic complementarity is yet to be widely exploited in the context of molecular crystal structures. We have recently demonstrated how the graphical representation of ab initio electrostatic potentials mapped on Hirshfeld surfaces can be used to rationalize patterns of intermolecular interactions in molecular crystals, with application to small cyclic molecules such as alloxan, benzonitrile and fluorobenzene [1]. Through application to a much wider range of molecular crystals incorporating weak and strong hydrogen bonds, halogen bonds, and C-H...pi and other weak interactions, we explore the extent to which electrostatic

complementarity is a widespread occurrence in the packing of molecules in crystals.

[1] M.A. Spackman, J.J. McKinnon, D. Jayatilaka, *CrystEngComm*, 10, 377-388 (2008)

Keywords: electrostatic potential, crystal engineering, intermolecular interactions

MS.46.1

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Structure and properties of ammonia borane based hydrogen storage materials

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Ammonia borane contains more than 19wt% hydrogen and has received significant attention as a promising hydrogen storage material. Although the decomposition temperature of NH_3BH_3 is relatively low, its propensity to release deleterious decomposition products such as borazine has mitigated against its development as a hydrogen storage material. Here we present results that show that improved thermal desorption parameters may be obtained when one of the protic hydrogens on the nitrogen is replaced by either a lithium or a sodium cation. Lithium and sodium amidoboranes have recently been shown to release two molar equivalents of H_2 at around 92°C . Structural analysis has shown that both LiNH_2BH_3 and NaNH_2BH_3 are isostructural and that the dihydrogen bond that is evident in ammonia borane is not present in these amidoboranes. We present neutron and X-ray powder diffraction measurements and provide a detailed comparison of ammonia borane with the alkali metal amidoboranes and other amidoboranes that show promising decomposition behaviour close to room temperature.

Keywords: hydrogen storage, *in-situ* powder diffraction, neutron and X-ray diffraction

MS.46.2

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Light metal borohydrides: Going beyond crystal structures

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Light borohydrides are considered as prospective materials for energy storage. However, due to their high stability they are not yet regarded being practical. In order to understand the stability and find ways to influence it we studied structure and transformations of some light borohydrides at various temperatures and pressures. New structures were solved from synchrotron powder diffraction data. Some complex cases include the simultaneous determination of a structure and a strong preferred orientation; solving a difficult structure in the space group $P1$; detection of the inversion symmetry breaking induced by ordering of hydrogen atoms. We show that hydrogen atoms can be accurately determined from synchrotron powder diffraction data measured with area detectors. Disorder of the borohydride groups and strong lattice anharmonicity were revealed from diffraction data measured at various temperatures. These phenomena, being ignored, lead to a failure of theoretical predictions

of structural stability of light borohydrides. Pressure-temperature phase diagram of LiBH_4 was studied by diffraction and mechanisms of phase transitions were analyzed using a phenomenological model. It suggests an existence of cation-anion layers in all four known LiBH_4 phases. This conclusion is not trivial from purely geometrical point of view, but it can find a rational crystal-chemical explanation. The relative complexity of LiBH_4 structures and of the P-T phase diagram can be linked with the directional interaction of the tetrahedral BH_4 groups with spherical metal atoms. We hypothesize that the directional $\text{BH}_4\cdots\text{M}$ interaction in metal borohydrides leads to a formation of anion-centered complexes, determining structures of individual phases and mechanisms of their polymorphic transformations.

Keywords: hydride structure, synchrotron powder diffraction, structural transformations

MS.46.3

Acta Cryst. (2008). A64, C83

Structural investigation of metal borohydrides by X-ray/neutron diffraction and computational study

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Metal borohydrides, $M(\text{BH}_4)_n$ (M : metal; n : valence of M), are promising candidates for hydrogen storage materials because they have high hydrogen gravimetric capacity (ex. LiBH_4 : 18.4mass%). Structural investigation of $M(\text{BH}_4)_n$ is an indispensable approach in order to understand their material properties. Whereas crystal structures of $M(\text{BH}_4)_n$ with $n = 1$ (alkali metal borohydride) have been clarified, those with $n \geq 2$ are, in many cases, still uncertain. So far, we clarified new crystal structures of $\text{Ca}(\text{BH}_4)_2$ (space group $Fddd$ (No. 70) with $a = 8.791(1) \text{ \AA}$, $b = 13.137(1) \text{ \AA}$ and $c = 7.500(1) \text{ \AA}$) [1], and $\text{Y}(\text{BH}_4)_3$ (space group $Pa-3$ (No. 205) $a = 10.771(4) \text{ \AA}$) [2], by using combination studies of powder x-ray/neutron diffraction and computation. Ca^{2+} and $[\text{BH}_4]^-$ arrangements of $\text{Ca}(\text{BH}_4)_2$ is a related TiO_2 -type (anatase), and Y^{3+} and $[\text{BH}_4]^-$ arrangements of $\text{Y}(\text{BH}_4)_3$ is a distorted ReO_3 -type. By using first-principles calculations based on the clarified crystal structures and estimated reactions $(1/2)\text{Ca} + \text{B} + 2\text{H}_2 = (1/2)\text{Ca}(\text{BH}_4)_2$ and $(1/3)\text{Y} + \text{B} + 2\text{H}_2 = (1/3)\text{Y}(\text{BH}_4)_3$, the heat of formation of $\text{Ca}(\text{BH}_4)_2$ and $\text{Y}(\text{BH}_4)_3$ were calculated to be -151 and -113 kJ/mol BH_4 , respectively. They are in good agreement with the correlation between heat of formation for $M(\text{BH}_4)_n$ and number of Pauling electronegativity of M [3].

[1] K. Miwa *et al.*, (2006). *Phys. Rev.* B74, 155122.

[2] T. Sato *et al.*, (2008). *Phys. Rev.* B77, 104114.

[3] Y. Nakamori *et al.*, (2006). *Phys. Rev.* B74, 045126.

Keywords: hydrogen storage, neutron X-ray diffraction, density functional theory

MS.46.4

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Powder diffraction investigations of a new class of rare-earth aluminum hydrides

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