

**P.08.01.5***Acta Cryst.* (2005). **A61**, C316**Transformable Single-Crystal Adsorbent Based on 1-D Coordination Polymer Skeletons**Satoshi Takamizawa, Graduate School of Integrated Science, Yokohama City University, Japan. E-mail: staka@yokohama-cu.ac.jp

Recently, we found a single crystal host,  $[M(II)_2(bza)_4(pyZ)]_n$  ( $bza$  and  $pyZ$  = benzoate and pyrazine,  $M = Rh$  and  $Cu$ ), which is suitable for the study of gas-containing structure through gas adsorption. They generated gas inclusion crystals by transition from a closed  $\alpha$  to an open  $\beta$  phase through the process of smooth physisorption; guest gases are adsorbed into the generated narrow channels of the  $\beta$  lattice. I will present a new convenient procedure for crystallizing gas into a co-single crystal state by putting the crystal adsorbent in a gaseous guest atmosphere, which is efficient to ascertain the exact molecular/atom structures with high resolution for included light aggregates.[1]

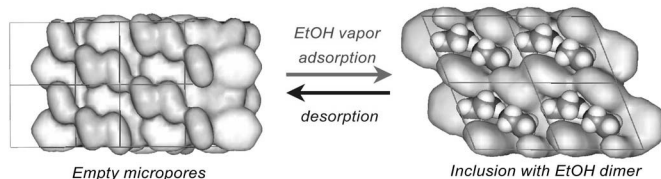


Fig. An example: ethanol dimer inclusion formation accompanying bulk phase transition.[2]

[1] a) Takamizawa S., et al., *Angew. Chem. Int. Ed.*, 2003, **42**, 4331.; b) Takamizawa S., et al., *Angew. Chem. Int. Ed.*, 2004, **43**, 1368-1371.; c) Takamizawa S., et al., *Inorg. Chem.*, 2005, **44**, 1362. [2] Takamizawa S., et al., *Inorg. Chem.*, 2005, **44**, 1421-1424.

**Keywords:** metal-organic complexes, porous materials, solid-state phase-transition

**P.08.02.1***Acta Cryst.* (2005). **A61**, C316**Is your Crystal Representative of the Bulk?**Howard D. Flack, G. Bernardinelli, University of Geneva, Switzerland. E-mail: Howard.Flack@cryst.unige.ch

Structure analysis by X-ray diffraction is commonly carried out on just **ONE** single crystal. The physical, chemical, pharmaceutical, biological and structural properties of this one crystal can only be characteristic of the bulk under certain circumstances. In particular for bulk samples which are mixtures, or whose purity is questionable, an excellent ploy is to characterize the one single crystal used for the diffraction experiment. However until recently a difficulty has been its small mass *ca.* 1  $\mu$ g. Thermochemical characterization by way of differential scanning calorimetry (DSC) can provide clear evidence on purity, phase transitions and solid-solution formation. For enantiomeric mixtures both circular dichroism (CD) and enantioselective chromatography, but not optical activity, may be applied to such a single crystal taken into solution.

As a first case study, a determination of absolute configuration was achieved from X-ray diffraction and CD measurements on crystals obtained from a racemate in the bulk by spontaneous resolution to give a tricky racemic conglomerate. Crystals were either enantiopure but twinned by a pure rotation or twinned by inversion in various proportions. In the second case study of an absolute-configuration determination from an enantiopure sample, the optical activity and CD spectrum were far too weak to be useful to characterize the enantiomer. However enantioselective chromatography on the single crystal taken into solution provided the necessary characterization.

**Keywords:** single-crystal, chiral, characterization

**P.08.02.2***Acta Cryst.* (2005). **A61**, C316**Model Wave Function for Glycyl-L-Alanine from Experimental Diffraction Data**Silvia C. Capelli<sup>1</sup>, Dylan Jayatilaka<sup>2</sup>, <sup>1</sup>Material Science Beamline at the European Synchrotron Radiation Facility, Grenoble, France.<sup>2</sup>Theoretical Chemistry, University of Western Australia, Nedlands, Australia. E-mail: capelli@esrf.fr

The XCW method is a relatively new technique for analysing X-ray diffraction experiments [1-5]. Rather than using the more common pseudo-atom expansion of the electron density [6], the X-ray diffraction data are introduced directly into the calculation of the quantum mechanical molecular wave function in such a way that the wave function is constrained to reproduce the X-ray data, at the expense of the smallest possible change in the quantum mechanical energy. The XCW method has been applied to a number of small-molecule organic crystals [2-4] showing, for example, that the constrained wave functions could model the effects of higher level calculations, simply by including experimental data or that the effects of the crystal lattice could be incorporated [2] and that a number of derived properties, such as electrostatic potentials and multipole moments could be obtained [3-4]. In order to address the limitations of the XCW method as compared to other forms of analysis of the electron distribution in crystals, like the pseudo-atom model, and to extend the application of the XCW method to more complex systems for which ab-initio calculations cannot be expected to give very accurate results (e.g. for proteins), synchrotron and neutron diffraction data have been measured on the model dipeptide Glycyl-L-Alanine at multiple-temperatures in the range 10 to 295K. The multi-temperature data were used in a molecular Einstein model [5] to get a more complete description of the thermal motion in the crystal and to recover information on the atomic correlation of motion. These latter were then included in the XCW fitting procedure to see their influence on the predicted structure factors and on the derived electronic properties. The neutron data were essential to evaluate the contribution of the motion of the hydrogen atoms to the final XCW-derived electron density.

[1] Jayatilaka D., *Phys. Rev. Lett.*, 1998,**80**(4), 798-801. [2] a) Jayatilaka D., Grimwood D. J., *Acta Cryst.* 2001, **A57**, 76-86; b) Grimwood D. J., Jayatilaka D., *Acta Cryst.* 2001, **A57**, 87-100. [3] Bytheway I., Grimwood D. J., Jayatilaka D., *Acta Cryst.* 2002, **A58**, 232-243. [4] Grimwood D. J., Bytheway I., Jayatilaka D., *J. Comp. Chem.* 2003, **24**(4), 470-483. [5] Bürgi H. B., Capelli S. C., *Acta Cryst.*, 2000, **A56**, 403-412.

**Keywords:** quantum crystallography, experimental wavefunctions, peptides

**P.08.03.1***Acta Cryst.* (2005). **A61**, C316-C317**Dynamics of Nucleoside and Nucleotide Hydrates by MD Simulation**Shigetaka Yoneda<sup>a</sup>, Yoko Sugawara<sup>a</sup>, Hisako Urabe<sup>b</sup>, <sup>a</sup>School of Science, Kitasato University, Sagamihara, Kanagawa. <sup>b</sup>Tokyo Kasei Gakuin University, Machida, Tokyo, Japan. E-mail: yoneda@sci.kitasato-u.ac.jp

Humidity-governed phase transitions of nucleoside and nucleotide hydrates are triggered by adsorption or desorption of crystal water molecules.[1] Lowering temperature, the phase transitions coupled with ordering of crystal water molecules in the hydrates were also observed. To know the dynamics of the phase transitions, we have started molecular dynamics simulation of hydrates of guanosine[2] and disodium inosine 5'-phosphate.

The simulation was performed with the AMBER 6 program in the periodic boundary conditions. The calculation cell was constructed to be about  $60 \times 60 \times 60$  Å by replicating the crystallographic unit in the directions of the  $a$ -,  $b$ -, and  $c$ - axes, respectively. The AMBER ff99 energy parameters and the TIP3P water parameters were used. Electrostatic interactions were calculated by the particle-mesh Ewald method.

Averaged structures, atomic displacement parameters, time profile of hydrogen bonding probability, formation of large translocation clusters etc. were analyzed based on the simulation trajectory. The origins of the phonons observed in Raman spectra[3] were also suggested.

[1] Sugawara Y., Nakamura A., Imura Y., Kobayashi K., Urabe H., *J. Phys. Chem. B*, 2002, **106**, 10363. [2] Yoneda Y., Sugawara Y., Urabe H., *J. Phys.*

*Chem. B.*, 2005, **109**, 1304. [3] Urabe H., Sugawara Y., Kasuya T., *Phys. Rev. B*, 1995, **51**, 5666.

**Keywords:** MD simulation, hydrates, nucleic acid

#### P.08.03.2

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#### A Novel Spin Transition Curve in [tris(2-picolylamine)Fe(II)]Cl<sub>2</sub> Allyl Solvate

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The title compound exhibits a temperature dependent spin crossover with an intermediate plateau in the spin transition curve (STC) around 111K at an unusual high-spin concentration of about 30%. This is well below the plateau with a 50% concentration observed for the isomorphous ethanol solvate [1].

We report here single crystal diffraction data collected at 200, 132, 111 and 94K. The systematic absences are consistent with *B*<sub>21</sub>/*c* space group symmetry at 200 and 132K. At 111K, *i.e.* in the range of the plateau, a superstructure is observed. The consequential reflections violate the original *B*-centering and lead to *P*<sub>21</sub>/*c* space group symmetry with a doubled unit cell volume. At 94K the original *B*<sub>21</sub>/*c* symmetry is recovered, thus indicating a reentrant sequence of phase transformations [2].

This observation shows that, as in the cases of the ethanol and 2-propanol solvates [1,3], a plateau in the STC reflects the appearance of a new ordered structure. The plateau region is likely a result of the coupling of the spin conversion with the concurrent conformational ordering of the crystal architecture.

[1] Chernyshov D., Hostettler M., Törnroos K. W., Bürgi H.-B., *Angew. Chem. Int. Ed.* 2003, **42**, 3825. [2] Chernyshov D., Bürgi H.-B., Hostettler M., Törnroos K. W., *Phys. Rev. B*, 2004, **70**, 094116. [3] *in preparation*.

**Keywords:** spin crossover, phase transition, order-disorder

#### P.08.04.1

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#### Solid State Synthesis and Characterization of Some Novel Sodium Rare Earth Phosphates

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Recently, much attention has been paid to the rare earth phosphates because of their potential applications for optical materials, including laser, phosphors, and more recently, anti-UV materials [1]. MOPO<sub>4</sub> type materials possess properties that make them potentially useful for catalytic, electronic and ion exchange applications[2].

In this work, Ln<sub>2</sub>O<sub>3</sub> (where Ln= La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb) were used as a rare earth source, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> was used as a phosphate source and Na<sub>2</sub>CO<sub>3</sub> was used as a sodium source to obtain sodium rare earth oxyphosphates. Reactants were heated at 1100 °C for 20 hours. X-ray diffraction patterns, IR and Raman analysis, SEM pictures and EDX analysis were taken for characterization. According to these results, structures of these products were compared with previous ones[2-3].

[1] Hirai H., Masui T., Imanaka N., Adachi G., *J. Alloys and Compounds*, 2004, **374**, 84-88. [2] Gönen Z.S., Kizilyalli M., Pamuk H.Ö., *J. Alloys and Compounds*, 2000, **303-304**, 416-420. [3] Uztielik- Amour A., Kizilyalli M., *J. Solid State Chem.*, 1995, **120**, 275-278.

**Keywords:** rare-earths, oxyphosphates, solid-state

#### P.08.04.2

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#### The Systems Li-Ho-P-O and K-Ho-P-O: A Study in Inert Atmosphere

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The phosphates with open frameworks are materials that are composed by (PO<sub>4</sub>) tetrahedral and by others polyhedral as octahedral (XO<sub>6</sub>) and dodecahedral (XO<sub>8</sub>) units. So, this structural conformation prove several applications of such materials as ionic conductors, ion exchangers, scintillating materials for gamma ray detection [1], catalysts [2], anticorrosive [3], etc. As part of our phosphates with open frameworks research, we study the phases present in the systems Li-Ho-P-O and K-Ho-P-O using different temperatures reaction and atmospheres. In this work, different phosphates compound like rare earth phosphate (Xenotime-type HoPO<sub>4</sub>), alkali metaphosphate (APO<sub>3</sub>, A= Li, K) and an alkali-rare earth pyrophosphate (LiHoP<sub>2</sub>O<sub>7</sub>) [4] were synthesized. These phases were characterized by X ray powder diffraction, differential thermal analysis and microscopy methods. A crystallochemistry study relating the crystal structures was performed.

[1] Natarajan S., Eswaramoorthy M., Cheetham A.K., Rao C.N.R., *Chem. Commun.*, 1998, 1561, and references there in. [2] Clearfield A., Thakurb D.S., *Applied Catalysis.*, 1986, 1. [3] Deyá M.C., Blustein G., Romagnoli R., Del Amo B., *Surf.Coat.Tech.*, 2002, 133. [4] Hamady A., Fauzi Zid M., Jouini T., *J.Solid State Chem.*, 1994, 120.

**Keywords:** phosphates, phase identification, X-ray diffraction

#### P.08.04.3

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#### Studies of Spin Crossover Complexes via Solvo-thermal Syntheses and their Thermal Relaxation of Light Excited Kinetic Phenomena

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The unique spin crossover 1D ladder complex [Fe<sub>2</sub>(bpt)<sub>2</sub>(NCS)<sub>2</sub>(bpy)<sub>2</sub>] · MeOH (**1**) have been synthesized successfully by one-step solvo-thermal syntheses or directly transformed from *trans*-[Fe(abpt)<sub>2</sub>(NCS)<sub>2</sub>] complex by hydrothermal process.

The magnetic measurement reveals that the 1D spin-crossover complex **1** has an abrupt spin transition at 130 K and possesses an unusual magnetic behavior. The π-π interactions of **1** do vary slightly with spin transition. The distances along the (110) and (101) planes are 3.65(1) Å and 3.52(5) Å at 295 K but 3.53(3) Å and 3.45(2) Å at 100 K.

The novel dinuclear Double bridging complex [Fe<sub>2</sub>(μ-bpt)<sub>2</sub>(NCS)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>](**2**) and [Fe<sub>2</sub>(μ-bpt)<sub>2</sub>(NCS)<sub>2</sub>(py)<sub>2</sub>](**3**) have also been synthesized and characterized by x-ray diffraction. The bond lengths of Fe-N are 2.292(3) Å, 2.094(3) Å for complex **2** and 2.110(2) Å, 2.321(2) Å for complex **3** at HS state.

The variable-temperature magnetic susceptibility measurement reveals that **2** and **3** are in high-spin state during 60-400 K. Interestingly, the complex **3** has a spin transition from HS to LS at low temperature under 808 nm radiation and the thermal relaxation behavior of such induced LS state will be discussed.

**Keywords:** LIESST, spin crossover, thermal relaxation

#### P.08.04.4

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#### Study of the Mechanism of Cu-Zn Mechanical Alloying by X-ray Powder Diffraction

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