important from the view points of solid-state chemistry and material sciences. We have been investigating the first-order phase transitions of nucleoside and nucleotide hydrates [1]. Conformational changes and shifts of molecular layers were observed coupled with increase or decrease of crystal water molecules. In addition, the transitions are characterized by hysteresis and emergence of metastable states.

One typical example is the transition of disodium 2´-deoxyguanosine 5´-phosphate (Na_2dGMP) between the tetrahydrate and the anhydrous forms. Besides hysteresis, bifurcation of phase transition was observed. The tetrahydrate transforms to two different anhydrous forms, A and B. The ratio depends on the transition temperature which is correlated to vapor pressure of water. In the reverse process, anhydrous form A transforms to the tetrahydrate directly. On the other hand, an intermediate state appears in the adsorption process of anhydrous form B as is the case of guanosine [2]. By comparison of the crystal structure of the tetrahydrate with those of anhydrous forms A and B, it is concluded that interfacial and strain energy contributions in the nucleation process at the transition point are dominant factors in bifurcation, hysteresis, and emergece of the metastable states observed in the phase transitions.

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Keywords: phase transitions, nucleotides, hydrates

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Spin-Peierls Transition in Halogen-Bridged Mixed-Valence MMX Chain Compounds
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One-dimensional halogen-bridged mixed-valence dinuclear metal complexes, MMX chain compounds, have attracted much attention because of their characteristic physical properties originating from strong electron-lattice interactions and electron correlation [1].

The SQUID measurements of the novel 1-D iodo-bridged mixed-valence dinickel(II,III) complexes, $Ni_2(RCS_2)_4I$ (R=Et, *n*-Pr), revealed that the magnetic susceptibilities abruptly drop to singlet states accompanying by the spin-Peierls transition around 45 K. The X-ray diffraction images measured using the LTV X-ray camera at the SPring-8 BL02B1 showed superlattice reflections corresponding to 2-fold repetition length of the MMX units below 40 K. Single crystal structure analysis of $Ni_2(EtCS_2)_4I$ at 26 K including the superlattice reflections revealed the distorted structure like the ACP states observed for the LT phase of $Pt_2(RCS_2)_4I$ (R=Et, n-Bu) [1].

[1] Mitsumi M., Kitamura K., Morinaga A., Ozawa Y., Kobayashi M., Toriumi K., Iso Y., Kitagawa H., Mitani T., *Angew. Chem. Int. Ed*., 2002, **41**, 2767.
Keywords: spin-peierls transition, 1-D mixed valence compound, synchrotron radiation crystallography

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Fe(II), Fe(III) and Co(II)-Complexes with Aromatic Nitrogen-Containing Ligands
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Spin crossover compounds change electronic state in response to external perturbations such as change in temperature, pressure or irradiation. Complexes of Fe(II), Fe(III) and Co(II) can exhibit spin crossover behavior combined with suitable ligands. In this work 2,6-bis(2-pyridyl)-4(1*H*)-pyridone (OHterpy) 4'-Chloro-2,2':6',2"-terpyridine (Clterpy), 2,3,7,8-Tetrakis(2-pyridiyl)pyrazino[2,3-g] quinoxaline (BL2), and 2,3,2',3'-tetrakis(2-pyridyl)-6,6'-biquinoxalinyl (BL3) are used as ligands to obtain new spin crossover compounds. The spin crossover and possible hysteresis effects are highly dependent on intermolecular interactions within the crystals; changing the counter ion or solvent can affect both the crossover temperature and the evolution of it, as well as the hysteresis properties. $[Co(II)(OHterpy)_2]X_2{\cdot}nH_2O$ exhibits spin crossover with X = ClO_4^- [1]. $[Co(II)(OHterpy)_2](NO_3)_2{\cdot}0.5H_2O$ was synthesized and crystals were obtained by slow diffusion of $Co(NO_3)_2{\cdot}6H_2O$ and OHterpy in methanol. The compound crystallizes in the triclinic space group P $\bar{1}$ with unit cell dimensions: a = 8.831 Å, b = 8.875 Å, c = 18.588 Å, α = 86.13º, β = 84.01º, γ = 89.00º. Co-N distances in this hexacoordinated complex are 1.893 Å for both Co-$N_{central}$, and vary from 2.069 to 2.086 Å for the four Co-N_{distal}. The data were collected at 153 K, and judging from the Co-N distances only, the compound is predominantly low spin at this temperature.

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Keywords: transition metal complexes, aromatic nitrogen-containing ligands, spin crossover

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Spin Crossover in Solvates of an Iron(II) Complex with Solvent Mixtures
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Recently it has been shown that the family of crystalline alcohol solvates of $[Fe^{II}(2\text{-pic})_3]Cl_2$ display a range of spin transition scenarios: two-step transitions with and without hysteresis (2-propanol and ethanol), continuous transitions (methanol, 2-butanol) as well as the absence of any spin crossover (1-propanol, *tert*-butanol) [1]. These findings raise the question about the properties of solvates crystallized from *mixtures* of two alcohols. We present the structures and magnetic properties of three such mixed solvates of $[Fe^{II}(2\text{-pic})_3]Cl_2$ as obtained from diffraction and SQUID measurements. The mixed 1-propanol:2-propanol and ethanol:2-propanol solvates show continuous spin transitions, while the methanol:ethanol mixture shows a two-step transition.

The thermal and positional disorder of the solvent molecules is found to be coupled with the spin conversion of the bi-stable $[Fe^{II}(2\text{-pic})_3]$ complex, an observation which will also be discussed theoretically.

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Keywords: spin crossover, phase transition, order-disorder

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Dopant Atom Influence on the α → β Phase Transition in Thermoelectric Zn_4Sb_3
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Zn_4Sb_3 is a high performance thermoelectric material with an extremely high thermoelectric Figure of Merit at relatively low temperatures. Furthermore, previous studies by Jet Propulsion Laboratory have shown that the thermoelectric Figure of Merit can be improved by doping Zn_4Sb_3 with Cd.

Zn_4Sb_3 exists in three crystalline forms; the α, β, and γ phase before melting at 841 K. Only the β-phase (stable between 263 and 765K) has good thermoelectric properties. It is therefore of interest to examine what effect the dopant atom substitutions has on the α → β phase transition.

Multi temperature data was measured on a series of M_xZn_4-xSb_3 (M = Hg, Sn, Pb, Mg, Cd) using the large Debye Scherrer camera at beamline BL02B2 at Spring 8 in Japan. The data have been Rietveld refined in order to follow the phase transition.

The physical properties of the samples were measured on a Quantum Design Physical Property Measurement System, to