

**MOLECULAR DYNAMICS STUDY OF A NANOTUBE:  
TRYPTOPHYLGLYCINE**

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Molecular dynamics (MD) simulation can be used to predict the behavior of complex crystal structures that contain material confined within nanotubes [G Hummer et al. Nature (2001) 414, 188] and organic compounds. [Y. Pan et al. Molecular Simulation, in press and Y Pan et al. Phys. Rev. B, in press]. The nanotube structures of tryptophylglycine were extensively studied [H. Birkedal et al. Angew. Chem Int. Ed (2002) in press]. MD simulations of this compound were carried out both with and without water within the nanotubes. In the simulation containing water, the system was heated to 450 K and cooled to 40 K starting from the experimental 120 K structure. Phase transitions were observed at 270 K and 370 K. Below 250 K, the system is ordered and water molecules are completely bonded to the tube. Some of the hydrogen bonds, that are connecting water molecules to the walls of the tube, start to break at 250 K. The number of hydrogen bonds decrease to 1/3 and 1/5 from 250 K to 310 K. Water melting is predicted at about 270K and boiling at about 370 K. The water molecules are disordered at temperatures above 270 K and can move large distances along the direction of the tube above 310 K. Another simulation without water carried out from 120 K to 520 K indicates a change from a positive to negative thermal expansion along the c-axis at about 280 K and a phase transition (loss of crystallinity) at 450 K. The simulation results are not only in good agreement with our experimental results but also provide detailed information on the mechanisms responsible for the physical behavior of this nanotube. Our results show that the water molecules are involved in the mechanism of negative thermal expansion in the system containing water.

**Keywords:** MOLECULAR DYNAMICS SIMULATION PEPTIDE  
NANOTUBE

**TEMPERATURE DEPENDENT SYNCHROTRON X-RAY POWDER  
DIFFRACTION STUDIES: Fe(II) SPIN CROSSOVER COMPLEXES**

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Spin transition is a phenomenon commonly encountered among coordination compounds of first-row transition metals and refers to the existence of two different spin states of the metallic ion, which may lead to two different structural configurations. In the current study spin state transition has been induced by thermal changes. Magnetic-susceptibility and Mossbauer measurements of Fe(*teeX*)<sub>6</sub>(BF<sub>4</sub>)<sub>2</sub> [*teeX*=1-(2-haloethyl)-tetrazole, X=halogen] have been carried out revealing various types of spin transition and their crystal structures have been determined at room temperature from synchrotron x-ray powder diffraction data using direct-space methods (Dova et al. Acta Cryst. B57, 2001, 531-538 and unpublished results). The packing of X=Cl, Br, I) is similar while the one of F differs. In order to see whether structural phase transitions occur during the spin transitions, x-ray powder diffraction patterns have been collected using a Debye-Scherrer camera and Imaging Plate detector at BL02B2 beamline of SPring8 (Japan Synchrotron Radiation Research Institute) at a series of temperatures from 300 K down to 90 K (30K for X=F). The unit cells out of these patterns have been determined. There is a contraction of the volume of 5-7% (depending on the compound) between highest and lowest temperature. The space groups at room temperature (*P*<sub>2</sub>/c for X= Cl, Br, I and *P*-1 for X=F) are retained throughout the transition. From the above it can be concluded that these thermal spin transitions are not accompanied by crystallographic phase transitions. In order to explain the spin crossover behavior the structure determination at several points of the transition is in progress.

**Keywords:** SPIN CROSSOVER, LOW-TEMPERATURE POWDER  
DIFFRACTION, STRUCTURE DETERMINATION

**AB INITIO STRUCTURE DETERMINATION OF A Cu(II)-SCHIFF  
BASE COMPLEX FROM X-RAY POWDER DIFFRACTION DATA**

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Crystal and molecular structure of a Cu(II)-Schiff base complex, Cu(C<sub>15</sub>H<sub>12</sub>NO<sub>2</sub>)<sub>2</sub>, has been determined *ab initio* using X-ray powder diffraction. High-quality X-ray powder diffraction data were obtained with a Siemens D500 diffractometer using monochromatic Cu K $\alpha$ 1 radiation ( $\lambda$ =1.5406 Å). The diffraction pattern was recorded under ambient atmosphere over the angular range 6-100° (2 $\theta$ ) with a step length of 0.02° (2 $\theta$ ). The first 20 lines of the X-ray powder pattern were indexed on the basis of a triclinic solution with high figures of merit using the program DICVOL91, i.e., M20=32 and F20=115 (0.0079, 22). The refined cell parameters were a = 11.928 (4), b = 12.210 (5), c = 9.330 (5) Å,  $\alpha$  = 102.54 (4),  $\beta$  = 111.16 (5),  $\gamma$  = 86.16 (4)°. Integrated intensities were extracted from the iterative pattern decomposition procedure using the program EXPO and subsequently used to solve the structure by the Patterson and Direct methods. But none of the solutions was successful in building a model structure. Finally the structure was solved in space group *P*-1 by direct-space Monte Carlo simulated annealing approach. First principles density functional theory (DFT) calculations were used to distinguish between four possible orientations for the O-C-CH<sub>3</sub> side chain. The structure corresponding to the lowest lattice energy showed fairly good agreement with the experimental powder diffraction pattern and was assumed to be the correct one. Refinement of the model structure using the program GSAS with common isotropic thermal parameters for the O, N and C atoms resulted in Rp=12.21, Rwp=14.56 and R(I,hkl)=11.57% for 125 parameters.

**Keywords:** AB-INITIO STRUCTURE, POWDER METHOD, DENSITY  
FUNCTIONAL THEORY

**RESTRAINED RIETVELD REFINEMENT OF MOLECULAR  
MATERIALS FOLLOWING AB INITIO STRUCTURE SOLUTION  
FROM POWDER DIFFRACTION DATA**

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Successful Rietveld refinement of molecular materials often requires a large number of restraints. Guidelines presented here provide objective criteria at which to aim during such restrained refinements. A method is described for the determination of suitable restraint values to maintain realistic intramolecular geometry and simultaneously achieve a minimal restraints contribution to the  $\chi^2$ . The guidelines are illustrated with the *ab initio* structure solution and refinement of two previously unknown molecular crystal structures of biological importance, vitamin K<sub>3</sub> (2-methyl-1,4-naphthoquinone) and tryptamine free base (3-(2-Aminoethyl)indole), using powder X-ray diffraction data.

**Keywords:** RESTRAINED RIETVELD REFINEMENT SIMULATED  
ANNEALING BIOLOGICALLY IMPORTANT MOLECULES