

**[Ni(H<sub>2</sub>O)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub>·(15-crown-5)·2H<sub>2</sub>O: An Uncommon Polymorphic System.** M.A. Siegler, X. Hao, S. Parkin, C. P. Brock, Dept. of Chemistry, Univ. of Kentucky, Lexington KY, 40506 USA.

Four phases of [Ni(H<sub>2</sub>O)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub>·(15-crown-5)·2H<sub>2</sub>O have been found between 90 and 294 K: an ordered phase below 198 K (IV,  $P2_1/c$ ,  $Z' = 1$ ), an unusual commensurately modulated superstructure between 198 and 227 K (III,  $B2_1$ ,  $Z' = 7$ ), a partially disordered phase between 227 and 283 K (II,  $P2_1/m$ ,  $Z' = \frac{1}{2}$ ) and a more disordered phase above 283 K (I,  $I2/m$ ,  $Z' = \frac{1}{4}$ ). Phase III was found metastable at 90 K and the structures of all phases have been determined. The phase sequence was found *via* differential scanning calorimetry and all phases are related by reversible solid-solid phase transitions with no loss of crystallinity.

In all phases, the three dimensional HO...H network is similar and best described as a 1-D chain and a 2-D plane of H-bonds. The 1-D chains are built by a set of H-bonds between 15-crown-5 and Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, whereas lattice water molecules and nitrate anions enable the propagation of H-bonds in 2-D planes. Interactions along 1-D chains may change through the phase sequence: some interactions between 15-crown-5 and Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> may be more favorable in phase IV and less favorable in phase II. Phase III is best understood as a transitional phase that is similar to phase IV in some regions and similar to phase II in other regions.

