The Many Crystal Forms of [M(15-crown-5)(H₂O)₂](NO₃)₂

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Five structure types have been found between 90 and 320 K for crystals grown near 295 K from aqueous solutions equimolar in 15crown-5 and $M(NO_3)_2$, M = Mg, Mn, Fe, Co, Cu, or Zn (12 structures). In the tetragonal form (P4₁, Z'=2; Mn and Co) water ligands and nitrate ions form a 3-D network of H bonds. The other four structure types have 2-D patterns of H bonds and are best understood as modulated variants of a basic structure. Two 2-D phases have been seen for each metal except Co; the phase pairs are all linked by reversible transitions during which the crystals remain single. The 2-D phases all have Z'>1: P2₁/c, Z'=3 (Mg, Mn, Fe, Zn); P2₁/n, Z'=5 (Cu), P2₁, Z'=8 (Mg, Fe, Zn), and P-1, Z'=2 (Mn, Cu).

In the 2-D phases, cations adjacent along the direction of the modulation are either essentially superimposable or enantiomeric. In the five transitions, which relate three different pairs of the four phases, the phase found at the higher temperature always has a larger value of V/Z and a more perfect pattern of enantiomeric alternation.

The values of Z' > 1 are a consequence of a conflict between the spacings of the *M* and nitrate ions most favorable for the formation of H bonds and the spacings most favorable for the close packing of the crown ligands. The reversible phase transitions are possible because inversion of the crown ligand does not require large atomic displacements. Analyses of the crystal packings show why 15-crown-5 ligands increase the probability that a structure will be disordered or modulated.

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