In the framework of the study of the precursor states preceding the crystalline structure transformation associated with a decomposition reaction of the type Solid 1 → Solid 2 + Gas, we have studied the dehydration reaction of Ba₃Co₄O₇, Ba₃Co₄O₇, Ba₂Z₂O₄ to BaCo₄O₇ (or 1/1 into 1/1/0). Precursor states of the structural transformation associated with a modification of the chemical composition of the initial compounds have been observed. 1/1/0 progressively looses water without any transformation of its crystalline structure into 1/1/0. It happens for various amounts of water lost depending on the water vapour pressure. If this pressure is sufficiently low, 1/1/0 can lose all its 2 water molecules and becomes anhydrous (01/1/0). The main framework of the crystalline structure of 1/1/0 is preserved during the loss of water. Neutron diffraction experiments show how the hydrogen behave during the dehydration.

04.2-7 EVOLUTION OF Ba₃Co₄O₇, H₂SO₄, XH₂O STRUCTURE IN RELATION WITH x. By G. Chain-Fleury, J. Bouillot, Institut Laue-Langevin, Grenoble, France and J.C. Martin, J.C. Niepce, Laboratoire de Réactivité des Solides, Fac. Sciences Mirande, Dijon, France

The structure correlation principle (Bürgi, H.M.; Dutitz, J.D.; Acc. Chem. Res. 1983, 16, 153-161) has been applied to five-coordinate zinc and nickel complexes in order to map the mechanism for a bimolecular ligand substitution reaction at typical tetrahedral- and square-planar centres. Evidence for the following mechanistic pathways is presented:

04.3-2 Simultaneous Double N-Inversion Pathway

M. Kaftruy and I. Agmon
Department of Chemistry, Technion - Israel Institute of Technology, Haifa, Israel

The pathway for simultaneous double N-inversion has been derived from geometric data given by crystal structure determinations of various compounds containing the 1,2,4-triazoldenedione ring. Bond lengths and angles in this fragment are functions of the degree of flattening at the two mutually-bonded N atoms. Two parameters were used to define the flattening at the N atom: the out-of-plane displacement of the N-N bond (δ) and the average of the valence angles at the N atom (α). Bond lengths and angles are linearly related to δ and logarithmically to α.

Extrapolation of the internal parameters according to their dependence on the degree of planarity, provides the fragment’s geometry at the transition state of the inversion. The results also show pronounced effect of the different substituents at the triazolidenedione ring.

Statistical treatment suggests that only three independent factors concerning three molecular centres dominate the change in the geometry of the molecular fragment during the inversion.