Modular description of complex crystal structures requires (a) a definition of categories that are more general than those of isotypes, homotypes, polytypes and homologues (polymorphs), (b) a definition of a measure of similarity of the (more or less distorted) derivative slabs/blocks to their archetype/aristotype.

Proposed classification categories higher than homologous series are the series of pleistotypes in which iso-homotypic or homologous structure portions combine with structural elements that differ from one member to another (they are called series of merotypes if these new elements are distinct types of interlayers).

Distortion of crystal structures can be quantified using the CN-dependent concept of "centroid" of the coordination polyhedron and the derived measures of cation eccentricity and polyhedron sphericity (Balic-Zunic & Makovicky 1996). In addition, we shall define a parameter-free measure of distortion of the coordination polyhedron away from its ideal shape. This measure involves calculation of the ratio of the volume of least-squares circumscribed sphere to the volume of the coordination polyhedron under study and the comparison of this ratio to a similar ratio for the ideal polyhedron. This measure works unambiguously for tetrahedra, octahedra and all other cases for which the number of polyhedral faces is constant. Distortion measures for the studied structures (fragment) are then compared those observed for the archetype/aristotype.

The more rigid environment appeared to impose more structure on disordered perchlorate ions in the crystal. This suggested that the perchlorate can be considered as structureless in solution and to assume [3] a tetrahedral shape in the solid state at a low temperature. An extensive search of the Cambridge Database revealed ordered and disordered perchlorates and it is not always easy to distinguish between the two instances. Investigation of the relationship of the free volume and the degree of disorder reveals that the larger the available space for the perchlorate ion, the higher the degree of disorder that results. A program [4] that calculates the volume of the molecule was then used to calculate the free available volume from the total cell volume. Comparisons of structures at room temperature and at low temperature demonstrate the relationship between the free volume available and the degree of disorder displayed by the perchlorate ion.

References: