

Stereoisomeric Behaviour of Octahedral $[^{6}M\emptyset_4]$ Chains

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Infinite chains of edge-sharing octahedra with the general stoichiometry $[^{6}M\emptyset_4]$ (where $\emptyset = O^{2-}$, $(OH)^-$, (H_2O) , Cl^- , or F^-) are present in over 175 mineral species with over 100 crystal structure types. These chains may be decorated with varying numbers of $T\emptyset_4$ tetrahedra and $D\emptyset_3$ triangles such that the complete stoichiometry of the corresponding mineral may be expressed as $A_xM_y(T\emptyset_4)_x(D\emptyset_3)_y\emptyset_z$ where A = a low-charge highly-coordinated cation, commonly an alkali or alkali earth, that is only weakly bonded to the chain, M = a high-charge cation in octahedral coordination, T = a high-charge cation in tetrahedral coordination, and D = a cation in triangular coordination. From a combinatorial perspective, a very large number of chain stereoisomers is possible; however, only a relatively small number of these chains are observed in actual minerals. Rather than forming a large number of structures with a large number of stereoisomers, we can see that Nature uses a small number of stereoisomers to construct a large number of structures by varying the degree and dimensionality of connectivity between the units, with rarely more than one chain type observed in a single structure.

Within a $[^{6}M\emptyset_4]$ chain, the shared edges of an octahedron may be related by the inversion centre, forming straight *trans-trans* chains, or by other symmetry operators, forming more complex, kinked chains with a mixture of successive *trans-cis* linkages. On average, the *trans-trans* chains have repeat lengths of two octahedra, corresponding to distances of ~ 6 Å, whereas the mixed *trans-cis* chains have variable repeat lengths. Either type of chain may occur isolated in the structure, bonded only to A-group cations. However, the relatively simple geometry of the *trans-trans* chains allows certain stereoisomers to link together directly, forming progressively more dense structures. This is exemplified by the behaviour of the *trans-trans* $M(T\emptyset_4)\emptyset_2$ chain, which occurs in over 50 different mineral species, all with chain axes oriented parallel to each other. This chain structure consists of $(T\emptyset_4)$ groups linking two apical oxygens of every second pair of adjacent octahedra. The $^{[M+M]}\emptyset$ anions are typically underbonded and may easily bridge to additional tetrahedra. Where the additional tetrahedron is not part of another unit, the chains are isolated, as is observed in the structures of brackebuschite and bushmakinite, amongst others. However, where $(T\emptyset_4)$ groups link to the $^{[M+M]}\emptyset$ of a second chain and, in turn, the $(T\emptyset_4)$ groups of the second chain link to the $^{[M+M]}\emptyset$ of the first chain, infinite sheets result by translating this configuration along one direction, and each chain is linked to two others. This is observed in the structures of tsumcorite and bermanite, amongst others. Conversely, where the $(T\emptyset_4)$ groups of the second chain bond to the $^{[M+M]}\emptyset$ of a third chain, usually with inter-chain bond directions differing by $\sim 90^\circ$, three-dimensional frameworks result by translating this configuration along the two directions, and each chain is linked to four others. This is observed in the structures of adelite and descloizite, amongst others. Hence, by considering the occurrence of topologically similar structural units, direct connections can be made between large numbers of minerals of complex structure.