

Function, S_n , that gives both the stoichiometry and aspects of the bond topology of the structures. We may thus write the structure-generating function, S_n , for the biopyrribole structures as follows: $S_n = X_i[M_{(3n-1)}\Psi_{2(n-1)}\{T_{2n}\Theta_{(3n-1)}^{\text{br}}\Theta_{2n}^{\text{ap}}\Theta_{2n}^{\text{t}}\}_2]$. This function generates: $n = 1$, the pyroxenes; for $n = 2$, the amphiboles; for $n = 3$, the triple-chain pyrriboles; for $n = 4$, $S_4 = X_i[M_{11}\Psi_6\{T_8\Theta_{21}\}_2]$; for $n = \infty$, the micas. Where $N = 2$, the general form of the T component is $\{T_{2n}\Theta_{5n+2}\}$ which corresponds to the T component of H-layers in the polysomatic H-O-H series in which the ribbons are linked laterally by [5]- or [6]-coordinated cations, D, which have the coordination $(D\Theta_4^{\text{ap}}\Phi_{0-1}^{\text{t}})$. The general formula for an H layer is $[D\Phi^{\text{ap}}\{T_{2n}\Theta_{3n-2}^{\text{br}}\Theta_{2n}^{\text{ap}}\Theta_{4n}^{\text{t}}\}\Phi_{0-1}^{\text{t}}]$, where Φ^{t} after the T component occurs on the outside of the H-layer and is involved in linkage between adjacent H-O-H sheets. The H-layer links via its apical anions to the O-layer, giving the general formula of an H-O-H sheet as $[M_{3n+1}D\Phi^{\text{ap}}\Psi_n\{T_{2n}\Theta_{5n+2}\}\Phi_{0-1}^{\text{t}}]$. These H-O-H sheets can link directly through the Φ^{t} anions of the $(D\Theta_4^{\text{ap}}\Phi_{0-1}^{\text{t}})$ octahedra, giving $S_n = X_i[M_{(3n+1)}\Psi_{2n}(D_2\Phi_2\{T_{2n}\Theta_{5n+2}\}_2)\Phi_{0-2}^{\text{t}}]$. This function generates: for $n = 1$, the group-1 TS-block structures; for $n = 2$, the astrophyllite-group structures; for $n = 3$, nafertisite: ideally $\text{Na}_2[\text{Fe}^{2+}_{10}\text{O}_2(\text{OH})_6(\text{Ti}_2\{\text{Si}_{12}\text{O}_{34}\})](\text{H}_2\text{O})_{0-2}$; for $n = \infty$, the micas.

We may combine the two generating functions (above) into a single function: $S_{(N+n)} = X_i[M_{(3n+2N-3)}\Psi_{2(n+N-2)}(D_{2(N-1)}\Phi_{2(N-1)}^{\text{ap}}\{T_{2n}\Theta_{(3n-N)}^{\text{br}}\Theta_{2n}^{\text{ap}}\Theta_{2N}^{\text{t}}\}_2)\Phi_{0-2(N-1)}^{\text{t}}]$ that gives all the above structures. This expression also generates mixed-ribbon polysomatic structures. $S_{(1,2+3)} = X_i[M_{13}\Psi_6\{T_{10}\Theta_{13}^{\text{br}}\Theta_{10}^{\text{ap}}\Theta_{4}^{\text{t}}\}_2]$ gives the chemical composition and structure of the mixed-chain pyrribole, chesterite: $\text{Mg}_4[\text{Mg}_{13}(\text{OH})_6\{\text{Si}_{10}\text{O}^{\text{br}}_{13}\text{O}^{\text{ap}}_{10}\text{O}^{\text{t}}_{4}\}_2]$, and $S_{(2,1+4)} = X_i[M_{17}\Psi_{10}(D_4\Phi_4\{T_2\text{O}^{\text{br}}\text{O}^{\text{ap}}\text{O}^{\text{t}}_{4}\}_2\{T_8\text{O}^{\text{br}}_{10}\text{O}^{\text{ap}}_{8}\text{O}^{\text{t}}_{4}\}_2)\Phi_{0-4}^{\text{t}}]$ gives the chemical composition and structure of the mixed-chain H-O-H mineral, veblenite: $\text{KNa}(\text{H}_2\text{O})_3[(\text{Fe}^{2+}_5\text{Fe}^{3+}_4\text{Mn}_6\text{Ca}\square)(\text{OH})_{10}(\text{Nb}_4\text{O}_4\{\text{Si}_2\text{O}_7\}_2\{\text{Si}_8\text{O}_{22}\}_2)\text{O}_2]$.

Keywords: topology, prediction, mineral

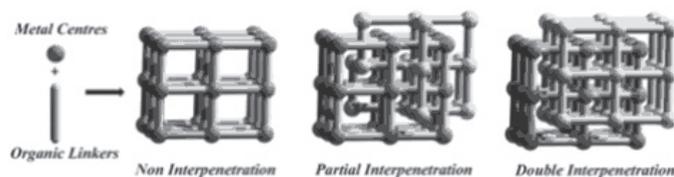
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Modulation of structures and gas storage properties in MOF materials

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A range of anionic metal-organic framework (MOF) materials has been prepared by combination of In(III) with tetracarboxylate isophthalate ligands. These materials incorporate organic cations, either $\text{H}_2\text{ppz}^{2+}$ (ppz = piperazine) or Me_2NH_2^+ , that are hydrogen bonded to the pore wall [1], [2]. These cations act as a gate controlling entry of N_2 and H_2 gas into and out of the porous host. Thus, hysteretic adsorption/desorption for N_2 and H_2 is observed in these systems reflecting the role of the bulky hydrogen bonded organic cations in controlling the kinetic trapping of substrates. Post-synthetic cation exchange with Li^+ leads to removal of the organic cation and the formation of the corresponding Li^+ salts. Replacement of the organic cation with smaller Li^+ leads to an increase in internal surface area and pore volume of the framework material, and in some cases to a change in the overall network topology and structure [3]. An increase in the isosteric heat of adsorption of H_2 at zero coverage has also been observed on incorporation of Li^+ ions, as predicted by theoretical modeling [4], [5], [6]. Furthermore, a new doubly-interpenetrated network system has been identified in which the second net is only partially formed (0.75 occupancy; see Figure). This material undergoes a structural re-arrangement on desolvation, and shows high selective storage uptake for CO_2 . The structures, characterisation and analyses of these charged porous materials as storage portals for gases are discussed.



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New findings in topological crystal chemistry with TOPOS

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The multipurpose crystallographic program TOPOS [1] has been used extensively in the analysis of entanglement of coordination polymers/MOFs and H-bonded supramolecular architectures [2], [3]. Three recent applications will be briefly illustrated.

We formalized the analysis of extended architectures by successive simplifications in an automated mode that allowed us to classify all 3-periodic structures from the Cambridge Structural Database (CSD). Different levels of representations (standard and cluster) are considered and some application illustrated. [4], [5].

Another new application of TOPOS is in the structural chemistry of intermetallic compounds, where the crystal structure is perceived as an ensemble of clusters based on convex polyhedra. We developed a computer procedure for fast automated searching for cluster fragments of any complexity in crystal structures of any nature [6]. The occurrences of two-shell clusters with the first shell as a Frank-Kasper polyhedron Z12 (dodecahedron), Z14, Z15, or Z16 (Frank-Kasper nanoclusters) will be briefly illustrated.

This latter approach has been extended in the study of zeolites, and from our result of description of all zeolites as natural tiling [7], we were able to develop a model of assembling zeolite-type frameworks as a packing of natural building units (minimal cages) or essential rings (minimal windows).

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