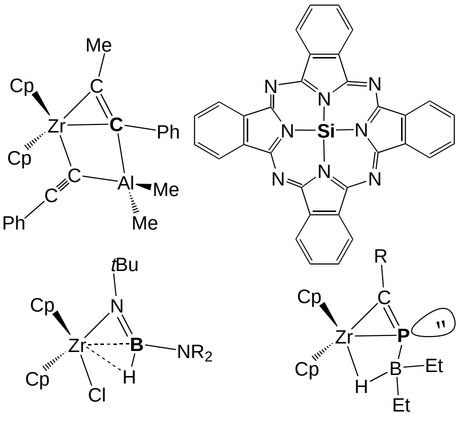

Scheme 1. Selected examples of compounds with atoms in “anti van't Hoff–Le Bel” configurations.

been reported for nitrogen or phosphorus.[8] However, if one considers a lone pair of electrons replacing a fourth substituent, then the phosphaalkyne complex adduct $[Cp_2Zr(RCP)(HBEt_2)]$ reported by Binger et al.[9] can be considered to contain a phosphorus atom in an “anti van't Hoff–Le Bel” configuration.

The strategy employed by Driess et al.[4] in the isolation of **1** may well have broad implications. Theoretical computations suggest that analogous “anti van't Hoff–Le Bel” geometries for SiR_4 and $[AlR_4]^-$ ($R = Zr(H)Cl_2$) may well be accessible. Similar calculations for ER_4 ($E = B^-, C, N^+$) infer a preference for a distorted tetrahedral geometry. However, it may be that other electropositive organometallic fragments will provide the requisite π-delocalization permitting access to a broader variety of compounds in “anti van't Hoff–Le Bel” configurations. While the preparative routes to other compounds containing these unusual geometries remains a synthetic challenge, this breakthrough prompts new and important fundamental questions regarding the effect of distorted geometries on the reactivity and reaction pathways. The discovery of this class of planar-tetracoordinate compounds does not supplant the 125-year-old notions of van't Hoff and Le Bel, rather, it describes exceptions to the “rules”, broadening our understanding of molecular structure. Perhaps more importantly, these efforts demonstrate that even long-standing tenets of a discipline must be questioned in an effort to more fully understand the fundamentals of the science.

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How Many Networks Can Be Made from Four-Coordinate Atoms?

Ulrich Müller*

In diamonds tetrahedrally coordinated atoms form a recurring, three-dimensional network. The same kind of network is found in cristobalite, with Si-O-Si groups taking the place of C–C bonds. A large number of other networks which consist of similarly joined tetrahedral building units are known among the polymorphs of SiO_2 and H_2O and especially among the zeolites.[1] In the network we can discern knots (Si atoms), edges (Si-O-Si bonds), and enclosed voids. The voids can be treated as tiles; a zeolite structure is then a three-dimensional recurring tiling. The tiles can have different shapes. For example, cubes, hexagonal prisms, β-cages (octahedra with cut vertices), and several others occur in zeolites. Every knot is joined with four other knots in a first sphere; in a second (and third, etc.) sphere, there may be different numbers of knots and they can be connected in different ways. For this reason, different kinds of knots can exist. Depending on the number of different kinds of knots the network is called uninodal, binodal, etc.

In two dimensions, there exist eleven different uninodal tilings, which already have been described by Johannes Kepler,[2] and 508 binodal tilings.[3] A procedure to calculate the numbers of possible tilings has been developed by the mathematician Dress and co-workers.[4, 5] Thus, the number of 508 was confirmed[6] and the number of possible trinodal two-dimensional tilings was calculated to be 16774.[7] Now the same research group has extended the procedure to three-dimensional tilings,[8] a fact that was even acknowledged in the daily newspapers. An essential part of the calculations deals with “Delaney symbols”. These allow the neighborhood of a tile to be designated in a concise way. The numbering of all recurring tiling amounts to the numbering of Delaney symbols.

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First results have been presented for networks having four-connected knots. In their consideration, "simple" and "quasi-simple" tilings are distinguished. This is a distinction that is somewhat contrary to the intuition of chemists. In a "simple" tiling every edge is common to exactly three tiles and at every vertex exactly three faces of a tile meet. The pattern is considered to be "simple" even if there are different kinds of tiles. Tiles for example can be cubes, tetrahedra, or prisms, but not octahedra. However, a packing of cubes, which a chemist would consider to be simple, is not "simple" (because an edge is common to four cubes).

For "simple" uninodal tilings there exist nine tilings, six of which correspond to known zeolite types and the other three have been described by O'Keeffe and Hyde.[9] Diamond, lonsdaleite (hexagonal diamond), cristobalite, gmelinite, cancrinite and further uninodal silicates belong to the 285 possibilities calculated for "quasi-simple" tilings with four-connected networks. Some structures, which from the mathematical point of view, are more complicated (neither "simple" nor "quasi-simple"), such as quartz, are not included in these numbers. The numbers of "simple" binodal und trinodal tilings were calculated to be 117 and 926, respectively; most of these do not correspond to a known structure. Two of them are shown in Figure 1. On the other hand, zeolites are known with up to 12 different kinds of knots.

The different views of what is taken to be "simple", depend on the starting point. For Dress et al. the tiles are the primary pieces, whereas chemists look essentially at the network of chemical bonds, at knots (atoms), and at coordination polyhedra (which are not tiles). For chemists (and crystallographers), the mathematical problem is not yet solved. Mathematicians can calculate exactly how many tilings are possible. However, the same network can result from some different tilings. The calculated 294 (9 + 285) "simple" and "quasi-simple" uninodal tilings correspond to only 154 or so four-connected networks. The exact number of networks can not yet be calculated; the research group of Dress is still trying hard to solve this. Furthermore, the procedure does not include crystal structures in which two separate networks of the same kind are interwoven, such as in Cu_2O.

The results contradict earlier calculations. Using graphs and "simulated annealing", Treacy et al.[10] found 6471 uninodal four-connected networks. However, they admit certain shortcomings in their procedure and state that their list is not complete. Unfortunately, Dress et al.[8] do not comment on this; they also do not cite the numerous earlier papers dealing with the systematic classification and numbering of structural possibilities of zeolites (and other networks), for example by Smith[11] or by Bosmans and Andries[12] (see refs. [10] and [12] for many other citations).

In a uninodal network the knots could be marked by different colors or be occupied by atoms of different elements, without changing the network itself. Thus far, the tilings have not been distinguished by such kinds of marking. Diamond, zinc blende, and chalcopyrite ($CuFeS_2$) have the same tiling and network, and are not distinguished. In crystal chemistry how many ways a network can be marked, that is how many crystal structure types can result from substitution, is indeed an important question. The numbering of possible substitution derivatives can be achieved with the aid of group theory and combinatorics, as has been known since 1974.

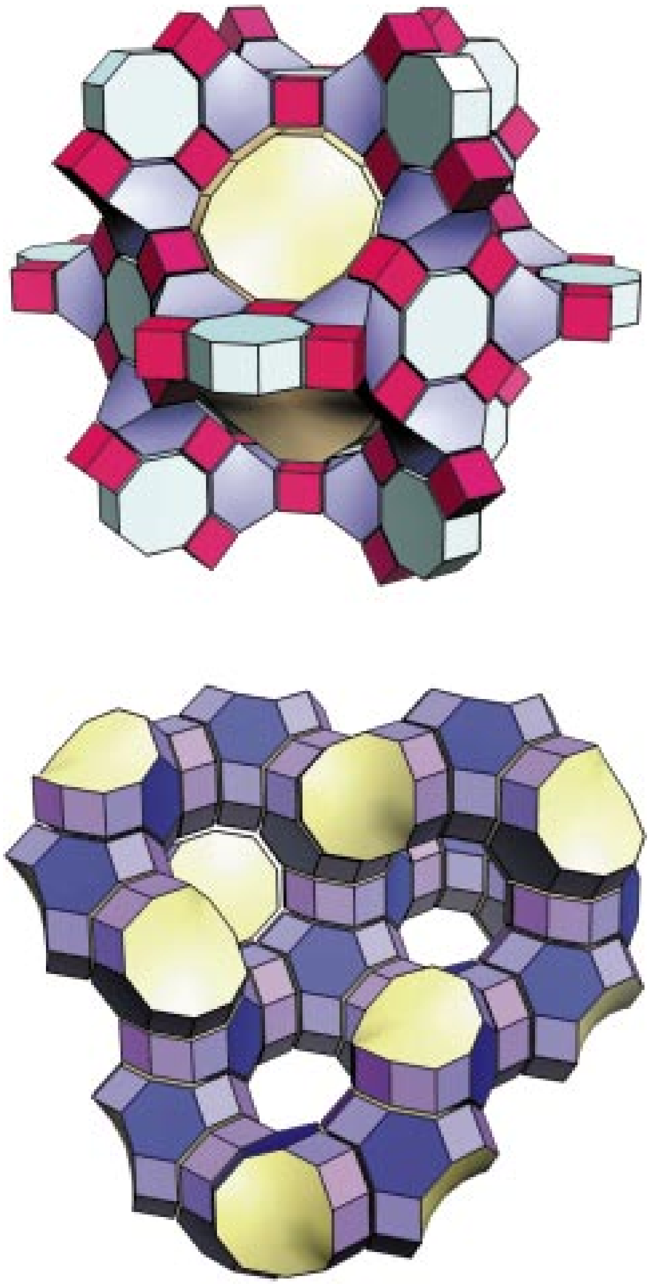

Figure 1. Two examples of the 285 possible binodal tilings (image by Delgado, reproduced with permission from ref. [8]; © 1999, McMillan Magazines).

Fortunately, the mathematical papers by White[13], hardly understandable for chemists, were translated into the language of crystallographers by McLarnan and are, thus, more easily accessible to our community. He also showed the application for sheet silicates, the stacking sequences for the closest packings of spheres, and the substitution derivatives of the wurtzite type;[14] for further details see ref. [15]. The starting point is the space group of the unsubstituted crystal structure (called aristo type). Substitutions involve symmetry reductions, resulting in subgroups of this space group. The subgroups which may occur can be derived by setting up a

Bärnighausen family tree of group–subgroup relations.[16] By using matrix algebra and some combinatoric rules with respect to the crystallographic positions of every space group, the numbers of possible structure types for each space group of the family tree can be calculated. The occupation of voids in atomic packing, as well as the production of vacancies, can be treated as a substitution of atoms for voids or vice versa; therefore, the method is not restricted to real substitution derivatives.

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