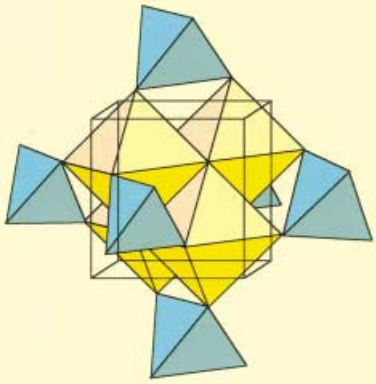
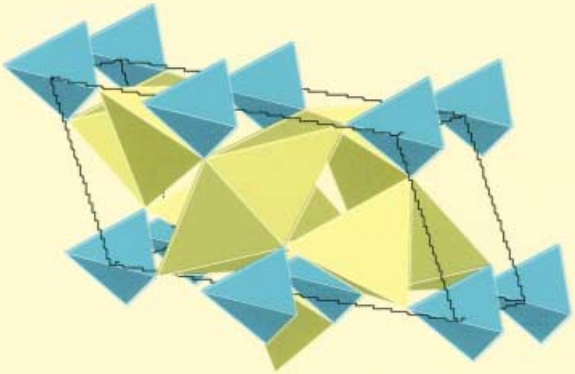
Computer Simulation of Structures



HP



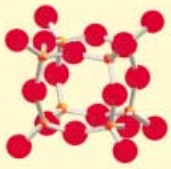
orthocarbonate
$[CO_4]^{4-}$

Not Yet Discovered

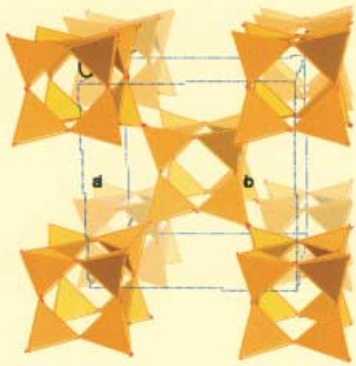
PRIMARY

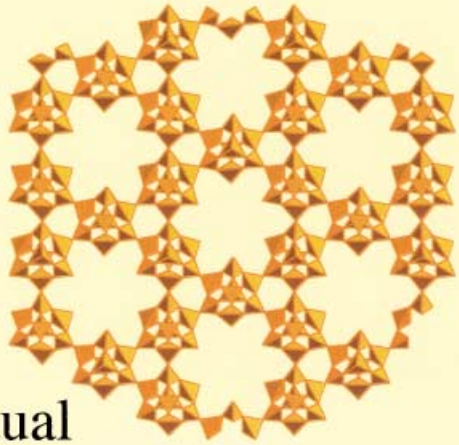
Aggregation of or **BUILDING UNITS**

SECONDARY



Real





Virtual

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Computational Design and Prediction of Interesting Not-Yet-Synthesized Structures of Inorganic Materials by Using Building Unit Concepts

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Abstract: The computational design of new and interesting inorganic materials is still an ongoing challenge. The motivation of these efforts is to aid the often difficult task of crystal structure determination, to rationalize different but related structure types, or to help limit the domain of structures that are possible in a given system. Over the past decade, simulation methods have continuously evolved towards the prediction of new structures using minimal input information in terms of symmetry, cell parameters, or chemical composition. So far, this task of identifying candidate structures through an analysis of the energy landscape of chemical systems has been particularly successful for predominantly ionic systems with relatively small numbers of atoms or ions in the simulation cell. After an introductory section, the second section of this work presents the historical developments of such simulation methods in this area. The following sections of the work are dedicated to the introduction of the building unit concept in simulation methods: we present simulation approaches to structure prediction employing both primary (aggregate of atoms) and secondary (aggregate of coordination polyhedra) building units. While structure prediction with primary units is a straightforward extension of established approaches, the AASBU method (automated asssembly of secondary building units) focusses on the topology of network-based structures. This method explores the possible ways to assemble predefined inorganic building units in three-dimensional space, opening the way to the manipulation of very large building units (up to 84 atoms in this work). As illustrative examples we present the prediction of candidate structures for Li_4CO_4, the identification of topological relationships within a family of metalphosphates, ULM-*n* and MIL-*n*, and finally the generation of new topologies by using predefined large building units such as a sodalite or a double-four-ring cage, for the prediction of new and interesting zeolite-type structures.

Keywords: building unit · computer chemistry · solid-state structures · structure prediction

Introduction

The challenging task of predicting crystal structures is of much current interest in materials science, chemistry, and crystallography.[1–6] Besides the desire to complement the traditional explorative aspect of solid-state chemistry by calculational routes,[5] the ever-growing demand for the design of new materials in various areas, such as superconductors, catalysts, nanoporous materials, ceramics, magnets, ferro-electrics, or biominerals, has driven the development of systematic approaches for the theoretical prediction of new compounds and their properties. For instance, in the area of microporous materials, this need is motivated by the recent trend to develop rational synthesis routes[7] dedicated to the design of new and interesting large-pore materials.[8]

Similarly, there is a growing interest in the design and representation of solids by using the concept of molecular building blocks, with the aim of rationalizing the synthesis of new inorganic materials in general. A whole series of recent articles[9] give an excellent picture of this still emerging field in solid-state chemistry aiming at producing predicted and not-yet-synthesized structures, by using intuitive and more rational a priori design approaches. As an illustrative example, the synthesis of new metal phosphates that contain four-membered rings has recently received particular attention, with the goal of possibly understanding the stabilization and the assembly of such units or related ones under hydrothermal conditions.[10] The authors demonstrate that such units may occur as precursors of metal phosphates synthesis with further self-assembly leading to more complex structures, ranging from one- to three-dimensional structures.

In such a context, the simulation of structures aims not only at simulating existing structures, but also predicting not-yet-

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synthesized topologies, their relation to existing ones, and their possible properties. The most general route to address this challenge starts from the observation that (meta)stable compounds are kinetically stable local minima of the free energy. This approach has been directly or indirectly behind all structure prediction and determination in chemistry, and we are going to elaborate on this in the next section.

Indeed, the prediction of periodic inorganic structures is a difficult task involving many degrees of freedom, which are related to the chemical and structural diversity of inorganic structures. Assuming, where appropriate, the occurence of specific building units, which incoporate chemical/structural information derived from known compounds, is a natural and valuable step towards the reduction of the number of degrees of freedom in the simulations. Therefore, there exists a large number of compounds for which one wants to simplify the exploration of the energy landscape of the system (i.e., the space of all possible spatial arrangements of all atoms) by introducing some structural information (e.g., prescribe a fixed size and shape of the unit cell) at the outset, and study the restricted landscape instead. For this purpose, one of the most useful concepts is the so-called "building unit" or "structural increment" that is well known from organic chemistry;[11] this is introduced as a rigid building block replacing many individual atoms and drastically reducing the space of parameters that needs to be explored.

Thus, it is not surprising that the computational de novo prediction of polymorphs by using such building units is now routinely explored in organic chemistry and polymer sciences.[6, 12, 13] Structures of organic molecular crystals have early-on been predicted with simulation tools that use symmetry constraints together with rules for assembling molecular entities based on simple intermolecular interactions, such as hydrogen bonding.[14, 15] However, such a task is evidently more difficult for inorganic networks and extended solids containing for example complex ions, due to the infinite extent of the crystal structures. For this reason, the prediction of not-yet-synthesized complex inorganic crystalline structures from minimal information is a relatively recent and still emerging research area.

In this work, we are going to apply the concept of building units to identify possible structures of not-yet-synthesized compounds. Our approach is twofold. Firstly, we are going to employ "primary" building units, which can represent both individual atoms and rigid collections of atoms such as molecules or complex ions. Their corresponding energy landscape can be studied by using generalizations of methods that have been successfully applied to structure prediction of solids employing individual atoms.[16] Examples will be given in the fourth section. However, for larger systems such as porous solids, more efficient methods are desirable. Therefore, in the third section, we present our recently developed AASBU approach[17] (automated assembly of "secondary" building units). The central feature of this new method is its use of the concept of building unit in a topological fashion: the combination of predefined building units and of empirical "glueing" rules allows us to scan the possible arrangements of such units in three-dimensional space to generate infinite crystal structures. Indeed, such a method opens the way to a topology-oriented search for new structures. Typically it has already allowed us to highlight topological relationships within groups of related materials, such as perovskites or bronzes.[17] Here, we have chosen to illustrate the application of the AASBU method in two areas of interest: 1) the identification of topological relationships within known families of complex inorganic structures (fifth section) and 2) the generation of new large-pore frameworks containing targeted local structures such as whole cages (sixth section).

Prediction of Inorganic, Infinitely-Extended Crystal Structures: History of the General Approach

Increasingly innovative and successful computational methods for simulating and predicting structures of inorganic solids have emerged in the past decade, with an unprecedented development of a collection of sophisticated simulation tools, ranging from minimization techniques, molecular dynamics, simulated annealing to first principles methods.

Regarding simulations of the structures of inorganic solids, atomistic simulations by using *local* minimization methods are extensively used in order to simulate the bulk, defect, and surface structures.[18, 19] One employs a microscopic model of the chemical system, in which the possible atomic configurations are exactly defined by the coordinates of every atom. Thus, every configuration of N atoms corresponds to a single point in a $3N$-dimensional configuration space. For each of these configurations, one can now compute the potential energy and its derivatives (forces on the atoms), and the hypersurface of the potential energy over the configuration space constitutes the so-called energy landscape of the system (for further details on energy landscapes, we refer to the literature, for example ref. [6]).

A crystal structure that is stable at 0 K corresponds to a local minimum of the potential energy in configuration space. Thus, structure prediction at low temperatures is essentially equivalent to the determination of all local minima, requiring a global exploration of the energy landscape. However, the atomistic simulation methods mentioned above usually restrict the exploration of the hypersurface of the energy to a very narrow region, for example the neighborhood of one or only a limited number of local minima. Thus, they require predefined (largely known) crystal structures in terms of space group, cell parameters, and atomic positions. They allow, for example, to refine or accurately reproduce crystal structures and explore their lattice energies, or to compare the energies of several minimum structures.

In the more challenging task of fully predictive simulations, we are interested in predicting both the existence (i.e., show their kinetic and thermodynamic stability) and the structures of not-yet-synthesized compounds. In this context, the real challenge consists in developing genuinely predictive computational procedures that generate physically and chemically plausible candidate structures, assuming minimum prior knowledge of the system of interest in terms of symmetry, cell-size and shape, electronic state, or even chemical composition. Here, *global* optimization techniques are required that are able to identify all local minima of the energy

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landscape and yield the corresponding candidate crystal structures.

Physically, a structure candidate capable of existence corresponds to a kinetically stable minimum of the free energy. As mentioned above, for low-temperature structures, this translates into potential-energy minima with sufficiently high "energetic" and/or "entropic" barriers. Finding all such minima requires the use of global optimization methods such as simulated annealing[20] or genetic algorithm methods,[21] and estimating their stability can be performed with additional exploration techniques, such as the lid method[22] or the threshold algorithm.[23] Indeed, due to their ability to cross barriers of the energy hypersurface and to search for regions with low-energy structures over a large volume of configuration space,[24] global optimization techniques are particularly effective methods for the generation of candidate structural models and have opened the way to the prediction of atomic-scale arrangements of inorganic structures.

For example, pioneer work has been done in the field of zeolites in the context of structure determination and refinement. Zeolites have early-on benefited from simulated annealing methods for solving zeolite structures from powder diffraction patterns.[25–27] Here, the generation of candidate structures obeys several externally imposed criteria, for example, cell-size together with symmetry and number of T-sites per unit-cell, with the use of an empirical cost function based on geometrical characteristics of zeotype structures. Typically, more than 5000 hypothetical structures can be generated with this method. Other related applications have consisted in the determination of the structure of already synthesized ionic or metallic compounds by performing a Pareto optimization, in which a weighted average of the potential energy and the agreement with a powder diffractogram of the compound is minimized.[28, 29]

Global optimization techniques require the use of an "energy" function that evaluates the suitability of the candidate structures. Regrettably, ab initio energy functions are too time-consuming to evaluate, and thus one usually employs a stepping-stone approach. Here, one evaluates the suitability of the candidate structures by assigning each atomic configuration an easily computed "cost" instead of the full potential energy, by using different kinds of cost functions (appropriately chosen for the particular type of chemical systems under investigation), during the first global search, followed possibly by a local energy minimization on ab initio level.

Most cost functions are approximations of the true potential energy, employing appropriate and validated interatomic potentials.[30, 6] However, sometimes additional terms are introduced reflecting either empirical chemical knowledge, such as the validity of the bond-valence rules, or the existence of geometric and/or topological requirements of the structural elements in the chemical system. For example, the bond-valence potential model was used for solving the structures of NbF_4 and K_2NiF_4[31] for a prescribed size and shape of the unit cell. As a result of the simulations, the sequence of the Nb–F and F–F radial distribution functions in NbF_4 during the simulated annealing process from the "molten" to the "frozen" crystalline state showed the emergence of the expected experimental NbF_4 structure. When coupled with lattice energy minimizations and appropriate potential-energy functions, like the Born model, simulated annealing based methods have allowed the exploration of the polymorphs of various chemical systems, such as noble gases,[32, 33] TiO_2,[34] SiO_2,[35–37] NaCl,[38] MgF_2,[39] Mg_2OF_2,[40] and alkali sulfides[41] and nitrides,[42] with no, or only limited, restrictions on the unit cell.

Another powerful alternative to simulated annealing methods has emerged with the use of genetic algorithms. Various binary/ternary oxides have been explored with this type of method[43, 44] for a fixed shape and size of the unit cell. Also, while not belonging to stochastic methods, enumerative approaches are largely used to classify and enumerate framework structures[45–49] given defined symmetry and connectivity constraints.[50] For further comparison, Table 1 gives a selection of the above atomistic simulation approaches successfully performed for generating inorganic models in the last ten years, with their respective characteristics, that is, the cost functions used and the input criteria imposed.

Interestingly, it is apparent from Table 1 that the development of simulation tools for crystal structure prediction has shown continuous improvements towards the use of a minimum amount of input data. From early work with rather drastic constraints (i.e., space group together with cell-parameters and chemical composition) needed to predict the atomic positions of, for example, zeotype candidate structures,[25–27] there has been a gradual reduction of the a priori knowledge needed to predict crystal structures.

For example, through the elimination of symmetry constraints during the simulations, Pannetier et al.[31] have opened the door to solve the following problem: given the chemical composition of a crystalline compound and the values of its unit-cell parameters, find its structure by optimizing the arrangement of ions, atoms, or molecules in accordance with a set of prescribed rules.

A further crucial improvement was achieved in subsequent work[5] in which chemical composition,[51, 33] ionic charge,[38] cell parameters,[32] and symmetry[32] are unconstrained during the global search. An illustrative application of this approach is the exploration of the energy landscape of hypothetical Mg_2OF_2 compounds.[40] First, structure candidates for Mg_2OF_2 were obtained through global optimization of the empirical potential energy by using a variable, periodically-repeated simulation cell containing up to four formula units (20 atoms). The neighborhoods of the corresponding local minima were explored with the threshold algorithm, yielding an estimate of the energy barriers among them and an analysis of their local density of states. For the most promising structure candidates, ab initio energy calculations were performed, in order to rank the various structure candidates. Finally, the composition of the magnesium oxide fluoride was varied from Mg_3OF_4 to $Mg_3O_2F_2$ and again global and local optimizations were performed, with the aim of gaining an insight into the shape of a hypothetical phase diagram. This analysis showed that 1) the preferred ternary composition should be Mg_2OF_2 and 2) this compound would probably be slightly metastable compared to a 1:1 mixture of the binary compounds MgO and MgF_2.

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Table 1. Structure prediction of inorganic solids: a selected comparison of characteristic features of simulation approaches.

Solids under study	Stochastic method[a]	Cost functions	Input data for simulations				Ref.
			Symmetry	Cell parameters	Chemical composition	Other	
zeolites	SA	figure of merit based on geometrical characteristics (d(T-T), a(T-T-T), etc.)	yes	yes	yes (i.e., number of T atoms/unit cell)	powder diffraction data	[25–27]
ionic/metallic compounds	SA	RB-value + simplified potential energy	**none**	yes	yes	powder diffraction data	[28,29]
NbF_4, K_2NiF_4, KAlF4, LiCoF4, $BaSiF_4$…	SA	bond valence model	**none**	yes	yes	–	[31]
SiO_2 polymorphs	SA	geometry and potential-energy function	**none**	yes	yes	–	[35–37]
Li_3RuO_4	GA	bond valence model + lattice energy (Born model)	**none**	yes	yes	–	[43]
TiO_2 polymorphs	SA	lattice energy (Born Model)	**none**	yes	yes	–	[34]
binary and ternary oxides (perovskites, pyrochlore, spinels…)	GA	refined bond valence model + lattice energy (Born model)	**none**	yes	yes	–	[44]
binary noble gases, binary and ternary ionic compounds (Na_3N, Li_3N, Ca_3SiBr, $SrTi_2O_5$, Mg_2OF_2,…)	SA + TA	potential energy (Lennard-Jones + Coulomb) + pV term + chemical potential)	**none**	**none**	**none**	optional: building units	[32,33,40]
octahedra-based structures: bronzes, perovskites, pyrochlore, NaCl, V_2O_6; zeotypes; complex SBUs: polymorphs of ULM-n	SA	auto-assembly potential function (Lennard-Jones)	optional	**none**	**none**	atomic model for building unit(s)	[17,53]

[a] SA = simulated annealing; GA = genetic algorithm; TA = threshold algorithm.

The Building Unit Concept

While these methods have been successful in dealing with, for example, classical ionic systems or porous materials under highly restrictive boundary conditions, they run into a variety of serious difficulties when dealing with situations in which different types of chemical bonds are present at the same time or in which the restrictions placed on feasible porous structures are lifted. Also, most of the methods discussed in the previous section assume prior knowledge of the exact chemical composition of the system under investigation, and require the use of specifically parametrized potential-energy functions to generate the solid of interest. Since the current approaches often operate within chemically or topologically constrained systems, such as in the case of zeolites,[25–27] they do not yet allow us to fully achieve the goal of predicting inorganic crystalline structures whatever their topology and independently of their chemical composition.

Here, the concept of a building unit serves as an important step forward, for which we distinguish between "primary" and "secondary" building units, each addressing a different class of problems. In the former case, the building unit is just a rigid aggregate of several atoms forming a molecule or a complex ion. Constructing such a building unit is equivalent to introducing large penalty terms in the energy/cost function that prevent the atoms in the aggregate from changing their relative positions. Apart from this, the same considerations hold as in the case of the exploration of the atom-based configuration space. In particular, the interactions among the atoms remain the same, for example, Coulomb and Lennard-Jones interactions, with the simplification that the intra-building unit interactions are constant and need no longer be evaluated explicitly during the optimization.[16]

In contrast, secondary building units are more abstract topological entities that can be used to construct a graph of corner-, edge-, and face-connected polyhedra embedded in three-dimensional space.[52] They are the foundation of our recently developed new approach, the AASBU method (automated assembly of secondary building units).[17, 53] The key feature of the method lies in the use of predefined topological building units and in the exploration of their auto-assembly in three-dimensional space through a sequence of simulated annealing plus subsequent minimization steps, with optional symmetry constraints, but leaving cell-parameters unconstrained.[54]

This computational method based on the abstract building units mentioned above has the great advantage that the simulations are independent of the chemical nature of the elements of the secondary building units (SBUs). This allows us to exclusively focus on their capacity to generate connections among each other, while automatically scanning structures related to one another through topological relationships. The rules that control the possible assembly of the SBUs are encapsulated in a cost function consisting of a Lennard-Jones-like term plus a "force-field" that favors "sticky-atom" pairs. However, this latter term has no direct physical meaning, serving simply to "glue" together the SBUs at the linkage points during the subsequent simulation steps, with a possible merger at a later stage of the graph generation.

The sequence of simulations provides a list of candidate structures together with their space groups, cell parameters, and atomic positions, that can, for example, be directly

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compared with existing inorganic structures. The feasibility of the method has been demonstrated through the generation of polyhedra "backbone" networks[55] of both known and not-yet-synthesized crystal structures among several large classes of solids, for example, perovskites, bronzes, zeolites, or spinnels.[17] Since no explicit limit regarding the nature, number, or size of the SBUs is involved, the method offers a boundless potential for exploration in terms of the topological diversity. This especially opens the way to the dedicated search for new and interesting structures, such as large-pore materials including cage or channel systems, identified through their expected properties (thermodynamic stabilities, adsorption capacities,…).

The following three sections are an attempt to illustrate the use of primary and secondary building units in the field of structure prediction. Previously unknown structures generated in this work will be referred to as "hypothetical" or "not-yet-synthesized" structures; however, we do not exclude the possibility that some of these "unknown" structures and/or structure types may have been previously conceived of or predicted using alternative methods.

Structure Prediction by Using Primary Building Units

Validation: A number of very different classes of systems have been investigated with the purpose of checking the applicability of primary building units as part of the global optimization.[16, 56] These range from simple molecules (for example N_2), over complex anions (e.g., NO_2 in KNO_2) to ions which can exhibit "non-spherical" charge distributions (e.g., Sn^{2+} in SnO). Both for N_2 and SnO, the low-temperature structures were the preferred local minima, while for KNO_2 many low-energy minima were found, which all corresponded to different modifications of the NaCl-type superstructure that is observed at high temperatures. In each of these modifications the NO_2 ion's rotation present at high temperatures is frozen in place thus breaking the high symmetry of the high-temperature structure.

Here, we are going to discuss another example, $MgCN_2$. Several Mg^{2+} ions and CN_2^{2-} ions served as the input. Associated with the building unit was a point charge distribution over the unit, with the total charges adding up to -2. The interaction was a Coulomb interaction among the charges of the Mg and CN_2 units plus a Lennard-Jones potential describing the repulsion and the polarization of neighboring atoms, similar to the one employed in the usual structure prediction with simple ions.[38] The positions of the nitrogen atoms of the building unit relative to the carbon atom were chosen to be the average of those observed in other dicyanamides. To avoid the introduction of further potential parameters, the building unit was treated as rigid. Since the final charge distribution within the CN_2^{2-} unit is not known a priori, global optimizations were performed with several distributions, $(q(C) = +4,\ q(N) = -3)$, $(q(C) = +2,\ q(N) = -2)$, $(q(C) = 0,\ q(N) = -1)$, and finally with the total charge (-2) located in the center of mass of the unit.

A large number of structure candidates was found, with the two most prominent ones being the experimentally observed structure and a structural analogue to the FeS_2 structure, respectively, in which Mg occupies the Fe positions and CN_2 replaces the S_2 dumbbells. Both structures appeared as local minima of the energy function for several of the charge distributions, indicating the high robustness of these configurations. For these two structure candidates, we performed local ab initio optimizations using the Hartree–Fock program CRYSTAL98[57] together with a shell code we wrote to perform an efficient local optimization. We found that the experimentally observed structure had the lower energy as expected, but that at very high pressures a transition to the FeS_2-related structure might be possible.

Structure prediction: As an example of structure prediction, we are going to consider the system Li_4CO_4. Here, lithium was chosen as Li^+, and we employed a CO_4^{4-} building unit, with two limiting charge distributions, $(q(C) = +4, q(O) = -2)$ and $(q(C) = 0,\ q(O) = -1)$, and a tetrahedral coordination analogous to SiO_4 units in crystalline SiO_2. Since this structural unit has not yet been observed within an extended solid, we have in addition optimized the size of the building units over a range of C–O distances, $d(C–O) = 1.37 – 1.57$ Å. The lower limit of the "bond length" was chosen to approximate the sum of the ionic radii of C^{4+} and O^{2-}, while the second one was based on the repulsion between the oxygen ions analogous to the one in SiO_4, which leads to a larger tetrahedron.

Again, the building unit was treated as rigid with fixed charge distribution for each individual optimization run, and the interaction between the ions was a sum of Coulomb and Lennard-Jones terms, just as in the case of the $MgCN_2$ system. The parameters of the Lennard-Jones potential were $\sigma_{LJ}(Li–O) = 2.1 – 2.2$ Å, $\varepsilon_{LJ}(Li–O) = 0.4$ eV. Up to four formula units were employed in these optimizations, and as usual cell size and shape, and atomic positions were free to vary. The adjustment of the size of the building unit occured by alternating empirical potential global optimizations and ab initio local cell optimizations for the structure candidates found in the global optimization step. The final C–O distance of $d(C–O) = 1.42$ Å is in satisfactory agreement with those experimentally and theoretically determined for molecules containing a CO_4 unit.[58]

After performing several hundred global optimizations in this fashion, six structure candidates turned out to be the most prominent ones (listed in Table 2).[59] They were found during optimization runs for nearly all sizes and charge distributions of the building unit indicating the robustness of these local minima on the energy landscape. In addition to these structure candidates, many further local minima were found in this system. In most instances, they either constituted distorted variants of the candidates discussed above or exhibited several different coordination polyhedra around the Li ions.

In some of the structure candidates Li was only fourfold coordinated in a distorted tetrahedron. These low-symmetry configurations are reminiscent of the (average) structure(s) given for Li_4SiO_4 in the inorganic crystal structure data base.[60] In this context, one notices the relatively high

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Table 2. Data for structure candidates for Li_4CO_4 after local optimizations on Hartree-Fock level using the CRYSTAL 98 program.[57]

Space group (no.), crystal system, type	Cell parameters (a,b,c [Å], α,β,γ [°])	Atom (multiplicity, Wyckoff letter), relative coordinates atom	x	y	Z	V_{min} [Å^3]	E_{min} [a.u.]
$P\bar{4}3m$ (215)	$a = 3.95370$	C (1b)	0.5	0.5	0.5	61.803	– 367.4492
cubic	$\alpha = \beta = \gamma = 90$	O (4e)	0.291988	0.291988	0.291988		
$Li_4(CO_4)$-**I**		Li (4e)	0.807997	0.807997	0.807997		
$R3m$ (160)	$a = b = c = 4.32264$	C (1a)	0.999612	0.999612	0.999612	79.821	– 367.4376
trigonal	$\alpha = \beta = \gamma = 84.7778$	O (3b)	0.819092	0.819092	0.193157		
$Li_4(CO_4)$-**II**		O (1a)	0.163217	0.163217	0.163217		
		Li (1a)	0.714089	0.714089	0.714089		
		Li (3b)	0.498611	0.498611	0.102857		
$I\bar{4}2m$ (121)	$a = 6.61036$	C (2b)	0	0	0.5	172.159	– 367.5417
tetragonal	$c = 3.93986$	O (8i)	0.624814	0.624814	0.791190		
$Li_4(CO_4)$-**III**	$\alpha = \beta = \gamma = 90$	Li (8i)	0.336138	0.336138	0.287824		
$I\bar{4}2m$ (121)	$a = 3.88482$	C (2a)	0	0	0	125.977	– 367.5620
tetragonal	$c = 7.89402$	O (8i)	0.705020	0.705020	0.603189		
$Li_4(CO_4)$-**IV**	$\alpha = \beta = \gamma = 90$	Li (8i)	0.176552	0.176552	0.648799		
Cm (8)	$a = 6.43641$	C (2a)	0.006574	0	0.496557	153.003	– 367.4973
monoclinic	$b = 6.50881$	O (4b)	0.999398	0.825902	0.713899		
$Li_4(CO_4)$-**V**	$c = 3.71019$	O (2a)	0.833148	0	0.214404		
	$\beta = 100.1426$	O (2a)	0.194344	0	0.353678		
	$\alpha = \gamma = 90$	Li (4b)	0.805456	0.694595	0.009318		
		Li (4b)	0.698232	0.198175	0.475248		
$C2$ (5)	$a = 8.25217$	C (2a)	0	0.197073	0	138.764	– 367.5888
monoclinic	$b = 4.27796$	O (4c)	0.366612	0.508428	0.021915		
$Li_4(CO_4)$-**VI**	$c = 4.37047$	O (4c)	0.578445	0.884280	0.289308		
	$\beta = 115.9229$	Li (4c)	0.257162	0.682776	0.294739		
	$\alpha = \gamma = 90$	Li (4c)	0.621522	0.134745	0.714904		

coordination numbers (mostly five and six) of Li by oxygen in several of the proposed structures, in contrast to the usual fourfold (and partly fivefold) coordination in for example Li_2O and Li_4SiO_4. Heuristically, the reason for this is most likely the size of the orthocarbonate ion: since it appears that it is about 10 – 15 % smaller than the analogous SiO_4 unit, the tetrahedral cavities that can be formed by the oxygen ions are too small to contain the Li ions, and thus the electrostatic and packing contributions to the energy appear to be better satisfied by an extended coordination sphere of the Li ion.

Figure 1 shows the final energy/volume curves taken from the local optimization on Hartree – Fock level. From this, we would conclude that the most likely structure will be Li_4CO_4-**VI** (Figure 2b), and at a pressure of about 5 GPa, a transition to the Li_4CO_4-**I** structure (Figure 2a) will take place. The other four candidates considered are expected to be metastable, but need to be taken into account, of course, since they

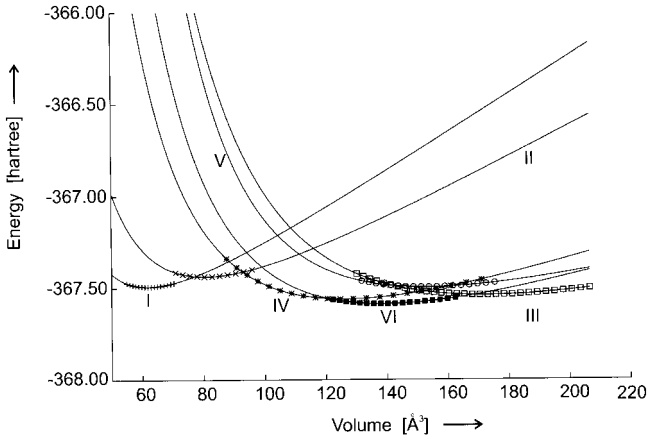

Figure 1. Energy/volume curves for Li_4CO_4 system. Plus signs: Li_4CO_4-**I**; crosses: Li_4CO_4-**II**; open squares: Li_4CO_4-**III**; asterisks: Li_4CO_4-**IV**; open circles: Li_4CO_4-**V**; filled squares: Li_4CO_4-**VI**.

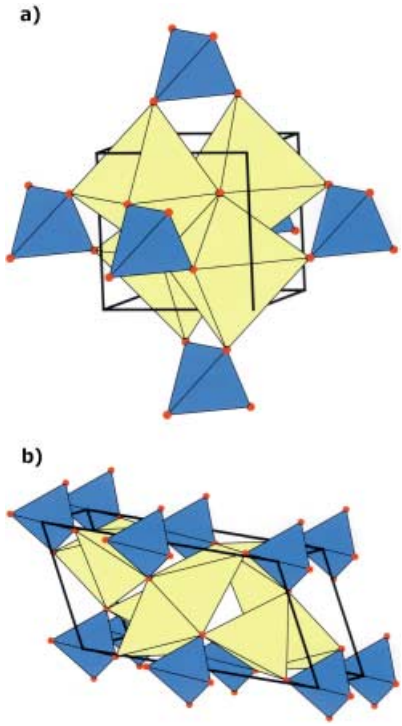

Figure 2. Structure candidates found during global optimizations of the Li_4CO_4 system, with CO_4 building units. a) Li_4CO_4-**I**: blue tetrahedra and yellow octahedra represent CO_4 and LiO_6 units, respectively; b) Li_4CO_4-**VI**: blue tetrahedra and yellow tetrahedra represent CO_4 and LiO_4 units, respectively. Red spheres represent oxygen atoms.

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(and many additional structures not listed here[61, 62]) are also capable of existing, and might actually be found as the outcome of particular synthesis routes. Regarding the kinetic stability of these structures, we have no quantitative data, since no threshold runs have been performed for this system. However, the fact that the Li_4CO_4-**I** and the Li_4CO_4-**VI** structures were found during global optimizations over a rather wide range of pressures and for all different sizes of the CO_4 unit, indicates they should possess a rather high degree of stability as long as the CO_4 unit itself is stable. Preliminary global optimizations for the Li_4CO_4 system employing carbon and oxygen atoms/ions instead of CO_4-units together with the lithium atoms/ions, show that for high pressures we should expect a shift in the coordination of carbon by oxygen from three (trigonally planar) to four (tetrahedral), suggesting that at sufficiently high pressures, the fourfold coordination will be stable.

Investigations of Topological Relationships: A Case Study of the ULM and MIL Families

By construction, the AASBU method turns out to be an ideal tool for generating and comparing structures which exhibit the same building unit but have different topologies. Here, emphasis is placed on the way building units are assembled to form the solid itself, and how this framework differs from one solid to another. Such a use of the AASBU method should allow us not only to rationalize the organization of the known structures, but also to search for new topologies based on the same building unit.

With this in mind, we have extensively investigated the ULM and MIL families of solids.[63] These compounds are obtained by hydrothermal synthesis and consist of fluorinated gallophosphates templated with various amines. Most of them are built from a hexameric unit (SBU-6) that contains three phosphate groups and three gallium polyhedra (one octahedron and two trigonal bipyramids) (Figure 3, bottom). Depending on the nature of the templating amine, different structures are obtained; the *trans*-corner linkage of the SBU-6 gives rise to layered structures with linear or zig-zag chains, such as ULM-8 and MIL-30, while connections of SBU-6 by translation and/or by a mirror plane operation lead to three-dimensional structures with open frameworks, typically ULM-3, ULM-4, TREN-GAPO, or MIL-31.

AASBU simulations were performed in various space groups, by using a double SBU-6, together with appropriate Lennard-Jones parameters to allow their assembly in three-dimensional space (Figure 3, top). Ligand atoms available for connection are represented in black, while those already involved in intra-building-unit bonds are represented in clear grey, and were appropriately parametrized to prevent further connections. For clarity in the presentation of our results, the conventional "+" or "−" sign is used to represent the orientation of the building units in the simulated structures, depending on the position of the central tetrahedron below (+) or on top (−) of the central octahedron (Figure 3, bottom).

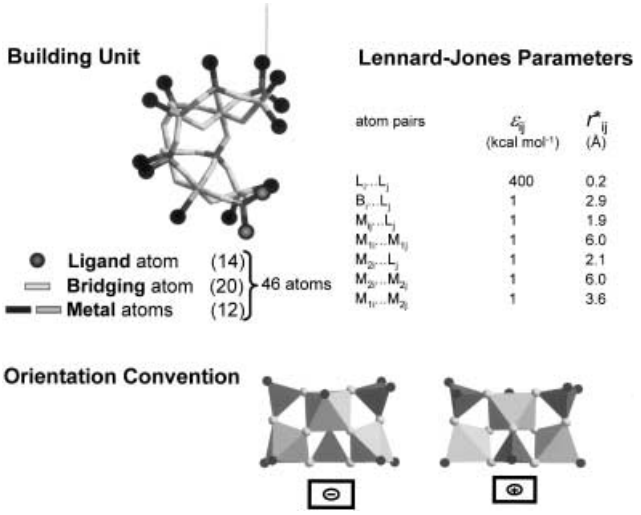

Figure 3. Bottom: The hexameric unit SBU-6 is extracted from experimentally known gallophosphates such as ULMs and MILs; it contains three phosphate tetrahedral groups (dark grey) and three gallium polyhedra (light grey). Ligand (i.e., connecting) atoms are shown as black spheres. Top: The double SBU-6 used in the AASBU simulations is shown together with the appropriate interatomic potential parameters that allow the connection of SBUs to one another.

The key result of the simulations is that not only the experimentally known topologies were predicted, but also a whole series of not-yet-synthesized topologies (see Figure 4). Interestingly, these simulated frameworks include both lamellar (two-dimensional) and three-dimensionally extended arrangements. It is noteworthy that in the cases of the experimental lamellar structures (ULM-8 and MIL-30), the template agents occupy the interlamellar space and are meant

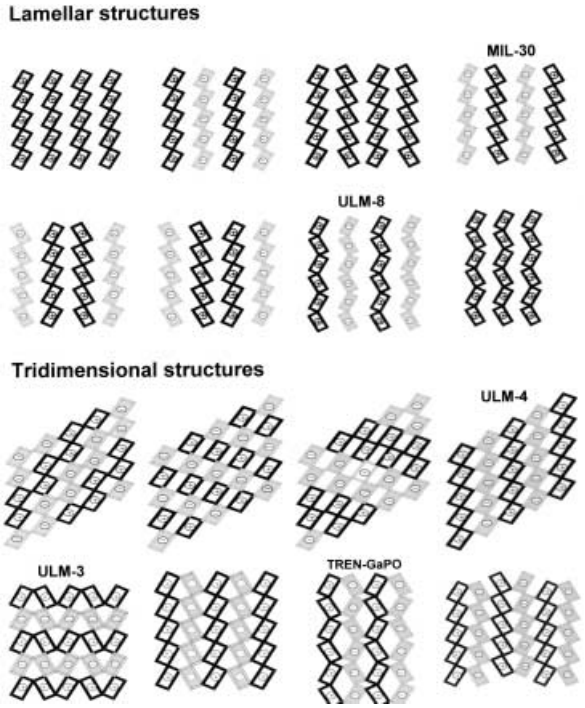

Figure 4. The AASBU simulations using the double SBU-6 (see Figure 3) generate both lamellar and three-dimensional structures, that include experimentally known topologies and not-yet-observed topologies.

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to influence the distances between the inorganic sheets. However, no attempt was made in our simulations to take into account the template agent and its interaction with the inorganic part. As a consequence, the distances between the sheets observed in the simulated lamellar structures have no chemical meaning, so that only the connections among the building units were analyzed and compared to those belonging to existing structures. For this reason, predicted space groups and cell parameters are given only for the simulated three-dimensional topologies.

Indeed, the prediction of a whole family of topologically related structures, including both known and unknown ones, demonstrates the efficiency of the AASBU method, and highlights the potential of this approach for structure prediction and determination purposes. In principle, such simulations allow us to build up a database of hypothetical structures, possibly based on relatively complex building units, that could be highly useful for solving the structure of related compounds synthesized in the future.

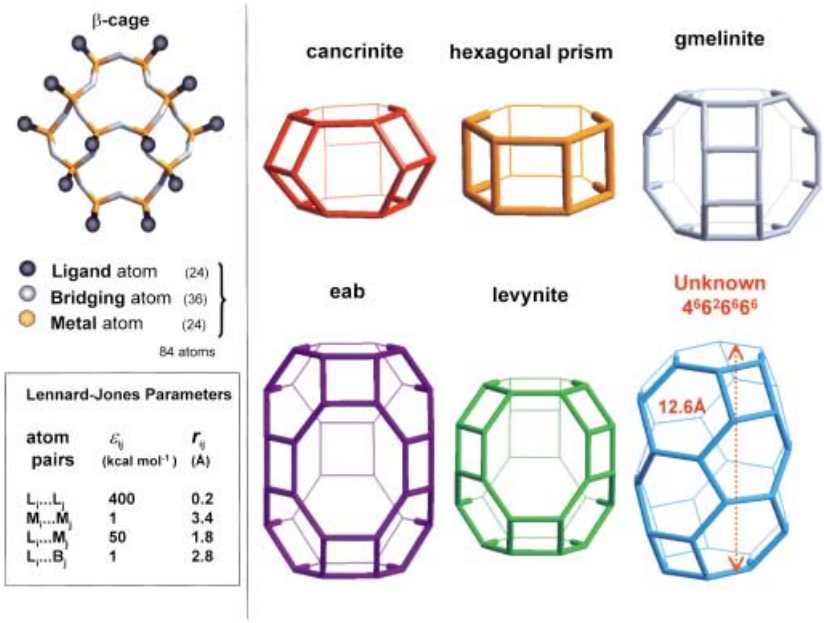

Figure 5. Left: The β-cage as extracted from the sodalite structure is used as a building unit. Ligand (i.e., connecting) atoms are shown as black spheres. Appropriate interatomic potentials are chosen to allow their connection during simulations. Right: the connection among β-cages during AASBU simulations produces a series of known (can, gme, eab, lev, hexagonal prism) and unknown (highlighted in blue) $4^6 6^2 6^6 6^6$ cages.

The Building Unit Used as Targeted Local Structure of Interest: Prediction of Materials Containing Sodalite and D4R Cages

In experimental chemistry, the building unit concept is evidently a very useful tool to a posteriori describe and analyze existing and new tolopogies, and in the preceding sections, we have used such units as input to structure prediction. Reversing this line of reasoning, there is a recent trend to consider the concept of building units as an a priori tool to reach synthetically targeted materials,[9] that is, postulate a given local structural unit and find extended structures that either incorporate or completely consists of such "target" units.

For this purpose, the AASBU method appears to be an excellent tool. As an interesting application in the area of microporous solids, we are going to use the AASBU method for the aggregation of large structural motifs, such as whole cages commonly found in known and interesting zeotype structures. Examples are the assembly of sodalite cages (β-cage) and double-four-rings (D4R), generating three-dimensional networks in the process.

Structures containing sodalite cages: As a first example, we chose the β-cage (Figure 5, left), which may be considered as the building unit of interesting zeotypes such as SOD, LTA, FAU, and EMT frameworks, that is, these structures may be described as being three-dimensional arrangements of only β-cages. Since a number of these zeolites have important industrial applications both in catalysis and gas separation, we expect that new structures built out of this cage may have interesting properties.

Prior to the AASBU simulations, the β-cage was extracted from the experimental sodalite structure,[64] leaving the first neighbor ligand atoms free for connection (in black in Figure 5). AASBU simulations were then performed in various space groups, by treating the β-cages as rigid bodies and by using appropriate Lennard-Jones potential parameters (Figure 5, left) to allow their joining. Sometimes, further relaxation of ligand atoms were achieved through additional minimization steps to allow full connection between β-cages.

Figure 6 shows a selection of three illustrative hypothetical frameworks, M_1, M_2, and M_3, generated by the AASBU simulations employing one β-cage per asymmetric-unit in space groups $C2/c$, $C2$, and Pm, respectively. These structures were produced along with their final space groups, cell parameters, and atomic positions. However, only the T-atom positions are indicated in Figure 6 for clarity, with β-cages highlighted in black in each hypothetical structure. Interestingly, while these unknown tolopogies evidently contain the targeted β-cage, the connections among the β-cages produce a whole series of known cage structures, such as cancrinite, gme, eab, lev, and hexagonal prism (Figure 5, right), together with previously unknown ones. Such an unknown cage appears in two of the hypothetical frameworks mentioned above, and was identified to be of type $4^6 6^2 6^6 6^6$ according to Smith's nomenclature[45] (Figure 5, right). It is also noteworthy that two of these hypothetical structures, M_2 and M_3, exhibit eight-ring channel systems, which are known to be a structural feature that is of interest for catalysis.

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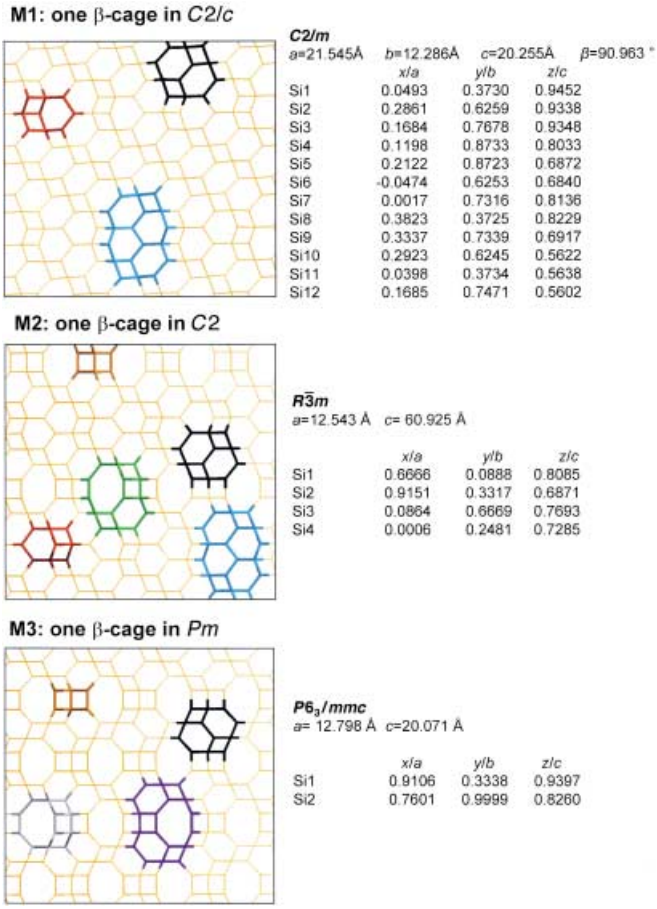

Figure 6. A selection of hypothetical frameworks produced during the AASBU simulations is shown here. In each structure, the β-cage is highlighted in black and other known/unknown cages in color. The two structures M1 and M2 contain the unknown cage $4^6 6^2 6^6$ (highlighted in blue).

This generation of hypothetical frameworks immediately raises the following question: what would be a compatible chemical composition for a given topology of interest? Finding an answer appears to be impossible using only current computational approaches. Thus, such an a posteriori choice of adequate chemical compositions currently requires the expertise of experimental chemists to rationalize the relationships between the corpus of already synthesized frameworks and their existing representatives in terms of chemical compositions. The occurrence of typical topologies within given chemical composition boundaries may provide hints for the synthesis of hypothetical frameworks. In this regard, simulations may be used to estimate the stability of hypothetical structures in various chemical compositions.

Following this line of reasoning, we have simulated the crystal structure, and estimated the lattice energies of six hypothetical zeotype frameworks, including M_1, M_2, and M_3, by using the GULP code[65] for energy minimizations, for three candidate chemical compositions SiO_2, $AlPO_4$, and $GaPO_4$, which are frequently reported for zeotype or related structures. The minimized lattice energy for each structure was normalized relative to the number of metal atoms in the structure and compared to the normalized lattice energy of their corresponding dense polymorphs, α-quartz (SiO_2), α-berlinite ($AlPO_4$), and $GaPO_4$-quartz, respectively, together with the energy of two existing topologies, the LTA- and SOD-type structures (Figure 7). The expected monotonic relationship between density and lattice energies is found, whatever the chemical composition. Interestingly, the hypothetical SiO_2 zeolite structures have lattice energies intermediate between the existing forms of SOD and FAU zeolites for pure silica. This suggests that such hypothetical structures may well be thermodynamically viable.

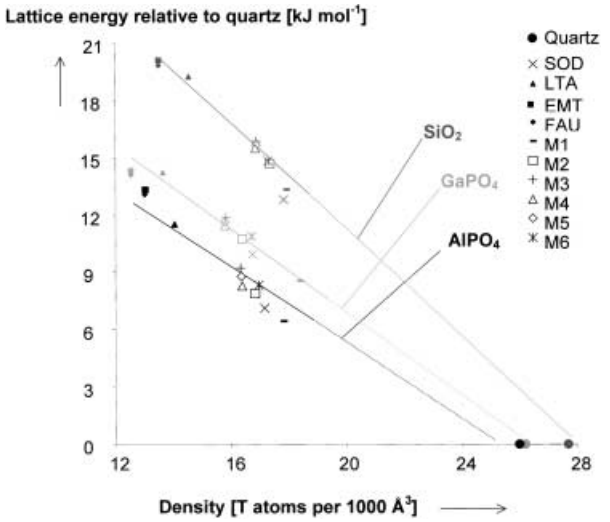

Figure 7. The minimized lattice energies of six hypothetical frameworks (M1–M6) are compared to those of five known structure-types (quartz, SOD, LTA, EMT, FAU) in three different chemical forms, SiO_2, $AlPO_4$, and $GaPO_4$. Following already known trends, a monotonic relationship is obtained between lattice densities and lattice energies.

Structures containing double four-rings: The synthesis of new structures containing D4Rs (double four-rings) have recently received particular attention, especially with the goal of identifying and understanding the stabilization of D4Rs and their assembly under hydrothermal conditions.[10, 66–68] Interestingly, known inorganic structures containing D4R range from three-dimensional frameworks, such as the one exhibited by cloverite[69] (known for its very open framework and its interesting acidic properties), to molecular arrangements of independent D4Rs, found, for example, in the recent example of [pyr,O]-GaPO-4 reported by Wragg et al.[10b] Both crystal structures are shown in Figure 8 (gray background), in which one D4R is highlighted in blue. Such a context has motivated our choice of the D4R as a building unit using the AASBU method, with the aim of searching for potentially interesting topologies, especially those possessing very open frameworks. Simulations were performed in various space groups, by using the D4R building unit as extracted from the experimental crystal structure of cloverite; the building unit therefore consists of a total of 28 atoms, including eight ligand atoms as connection points (Figure 8, upper left).

A selection of three hypothetical structures generated by the simulations are shown in Figure 8 (white background), all exhibiting interesting open topologies. For each structure, the final space group is indicated together with its cell parameters.

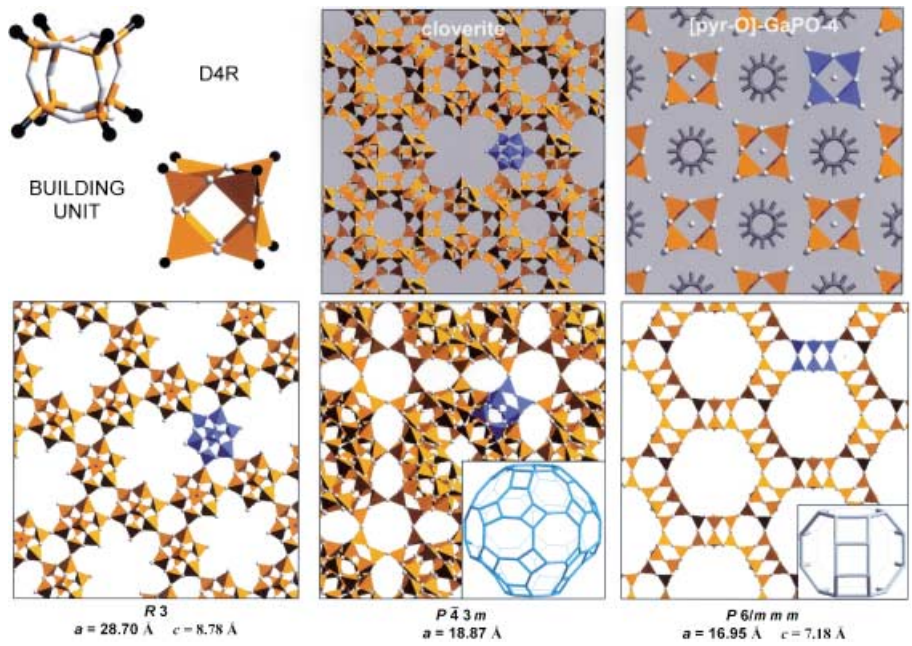

Figure 8. The double four-ring, D4R, participates in the framework of known structures (gray background). A selection of new and interesting frameworks (white background) generated by AASBU simulations using the D4R as a building unit is shown here. In all structures, the D4R unit is highlighted in blue.

For example, one of the structures (left) is closely related to the cloverite topology. Here, the tunnels are delimited by six D4R units, instead of eight in the cloverite structure. Its "interrupted" framework similar to that of cloverite, that is, containing "pending" oxygen atoms pointing toward the channel, suggests that such a new structure could have interesting catalytic applications involving acid sites. Another hypothetical structure (Figure 8, middle) contains the surprisingly large TSC[64] cage ($4^{24}6^{8}8^{18}$), with a free internal diameter of 16.2 Å. The third structure reveals the three-dimensional arrangement of D4R units generating regular 18-ring channels interconnected by gmenelite ($4^{3}4^{6}6^{2}8^{3}$) cages. Again, the question of the appropriate chemical composition required for stabilizing such low-density frameworks remains an open challenge.

Conclusion

As illustrated in the above examples, the use of primary and secondary building units in the exploration of the energy landscape of chemical systems allow us to greatly extend the range of our search procedures to include compounds with mixed bonding and large (covalent) networks. Besides the choice of the chemical system and the building unit(s), no additional information is needed, although for reasons of efficiency, one might want to keep the number of building units (and for the AASBU method optionally the symmetry) fixed for each individual optimization. The significant and new advantage of methods using such units is that the building unit may encapsulate a targeted local structure ranging from complex ions to whole cages or even possibly channels. This allows us a focussed search for new structures and network topologies, with as the final goal the design of a priori structures that possess predefined desirable properties such as a high catalytic activity in large pores.

Acknowledgement

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[1] J. Maddox, *Nature* **1988**, *335*, 201.
[2] M. L. Cohen, *Nature* **1989**, *338*, 291.
[3] F. C. Hawthorne, *Nature* **1990**, *345*, 297.
[4] C. R. A. Catlow, G. D. Price *Nature* **1990**, *347*, 243.
[5] J. C. Schön, M. Jansen, *Angew. Chem.* **1996**, *108*, 1358; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1286.
[6] J. C. Schön, M. Jansen, *Z. Kristallogr.* **2001**, *216*, 307; J. C. Schön, M. Jansen, *Z. Kristallogr.* **2001**, *216*, 361.
[7] D. E. Akporiaye, *Angew. Chem.* **1998**, *110*, 2594; *Angew. Chem. Int. Ed.* **1998**, *37*, 2456.
[8] G. Férey, A. K. Cheetham, *Science* **1999**, *283*, 1125.
[9] M. O'Keeffe, O. Yaghi, *J. Solid. State. Chem.* **2000**, *152*, 1; M. O'Keeffe, *J. Solid. State. Chem.* **2000**, *152*, 3; G. Férey, *J. Solid State. Chem.* **2000**, *152*, 37; see also: *J. Solid. State. Chem*, Special Issue, **2000**.
[10] a) C. N. R. Rao, S. Natarajan, A. Choudary, S. Neeraj, A. A. Ayi, *Acc. Chem. Res.* **2001**, *34*, 80; b) D. S. Wragg, R. E. Morris, *J. Am. Chem. Soc.* **2000**, *122*, 11246.
[11] E. J. Corey, *Pure Appl. Chem.* **1967**, *14*, 19.
[12] P. Verwer, F. J. J. Leusen in *Reviews in Computational Chemistry, Vol. 12* (Eds.: K. B. Lipkowitz and D. B. Boyd) Wiley, New York, **1998**, pp. 327–365, and references therein.
[13] R. J. Gdanitz in *Theoretical Aspects and Computer Modeling*, (Ed.: A. Gavezzotti) Wiley, New York, **1997**, pp. 185–201.
[14] W. T. M. Mooij, B. P. van Eijck, J. Kroon, *J. Am. Chem. Soc.* **2000**, *122*, 3500.
[15] J. P. M. Lommerse, W. D. S. Motherwell, H. L. Ammon, A. Gavezzotti, D. W. M. Hofmann, F. J. J. Leusen, W. T. M. Mooij, S. L. Price, B. Schweizer, M. U. Schmidt, B. P. van Eijck, P. Verwer, D. E. Williams, *Acta Crystallogr. Sect. B* **2000**, *56*, 697.
[16] J. C. Schön, M. Jansen, *Acta Crystallogr. Sect A* **1999**, *55*, Supplement.
[17] C. Mellot-Draznieks, J. M. Newsam, A. M. Gorman, C. M. Freeman, G. Férey, *Angew. Chem.* **2000**, *112*, 2358; *Angew. Chem. Int. Ed.* **2000**, *39*, 2270.
[18] *New Methods for Modelling Processes Within Solids and at Their Surfaces* (Ed.: C. R. A. Catlow), Oxford University Press, London, **1993**.
[19] *Computer Modelling in Inorganic Crystallography* (Ed.: C. R. A. Catlow) Academic Press, San Diego, **1997**.
[20] S. Kirkpatrick, C. D. Gelatt, M. P. Vecchi, *Science* **1983**, *220*, 671.
[21] *Adaptation in Natural and Artificial Systems* (Ed.: J. H. Holland), University of Michigan Press, Ann Arbor, **1975**.
[22] P. Sibani, J. C. Schön, P. Salamon, J.-O. Andersson, *Europhys. Lett.* **1993**, *22*, 479.
[23] J. C. Schön, H. Putz, M. Jansen, *J. Phys.: Condens. Matter* **1996**, *8*, 143.
[24] This ability to move over large distances on the landscape exploring very different classes of structures constitutes an important advantage over the use of for example molecular dynamics for optimization purposes.
[25] M. W. Deem, J. Newsam, *Nature* **1989**, *342*, 260.
[26] M. W. Deem, J. Newsam, *J. Am. Chem. Soc* **1992**, *114*, 7189.

  0947-6539/02/0818-4112 $ 20.00+.50/0

[27] M. Falcioni, M. W. Deem, *J. Chem. Phys.* **1999**, ***110***, 1754.
[28] H. Putz, J. C. Schön, M. Jansen, *J. Appl. Crystallogr.* **1999**, *32*, 864.
[29] A. A. Coelho, *J. Appl. Crystallogr.* **2000**, *33*, 899.
[30] T. S. Bush, J. D. Gale, C. R. A. Catlow, P. D. Battle, *J. Mater. Chem.* **1994**, *4*, 831.
[31] J. Pannetier, J. Bassas-Alsina, J. Rodriguez-Carvajal, V. Caignaert, *Nature* **1990**, *346*, 343.
[32] J. C. Schön, M. Jansen, *Ber. Bunsen-Ges.* **1994**, *98*, 1541.
[33] H. Putz, J. C. Schön, M. Jansen, *Ber. Bunsen-Ges.* **1995**, 99, 1148; H. Putz, Dipl. thesis, University of Bonn, **1994**.
[34] C. M. Freeman, J. M. Newsam, S. M. Levine, C. R. A. Catlow, *J. Mater. Chem.* **1993**, *3*, 531.
[35] M. B. Boisen Jr., G. V. Gibbs, M. S. T. Bukowinski, *Phys. Chem. Miner.* **1994**, *21*, 269.
[36] D. M. Teter, G. V. Gibbs, M. B. Boisen Jr., D. C. Allan, M. P. Teter, *Phys. Rev. B.* **1995**, *52*, 11.
[37] M. B. Boisen Jr., G. V. Gibbs, M. O'Keeffe, K. L. Bartelmehs, *Microporous Mesoporous Mater.* **1999**, *29*, 219.
[38] J. C. Schön, M. Jansen, *Comput. Mater. Sci.* **1995**, *4*, 43.
[39] M. A. C. Wevers, J. C. Schön, M. Jansen, *J. Solid State Chem.* **1998**, *136*, 223.
[40] H. Putz, J. C. Schön, M. Jansen, *Comput. Mater. Sci.* **1998**, *11*, 309.
[41] J. C. Schön, M. A. C. Wevers, M. Jansen, *J. Mater. Chem.* **2001**, *11*, 69.
[42] M. Jansen, J. C. Schön, *Z. Anorg. Allg. Chem.* **1998**, *624*, 533.
[43] T. S. Bush, C. R. A. Catlow, P. D. Battle, *J. Mater. Chem.* **1995**, *5*, 1269.
[44] S. M. Woodley, P. D. Battle, J. D. Gale, C. R. A. Catlow, *Phys. Chem. Chem. Phys.* **1999**, *1*, 2535.
[45] J. V. Smith, *Chem. Rev.* **1988**, *88*, 149 and references therein.
[46] M. O'Keeffe, B. G. Hyde, *Philos. Trans. R. Soc. London Ser. A* **1980**, *295*, 38.
[47] M. O'Keeffe, N. E. Brese, *Acta Crystallogr. Sect. A* **1992**, *48*, 663.
[48] J. Klinowski, *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 79 and references therein.
[49] J. Klinowski, *Nature* **1999**, *400*, 644.
[50] M. M. J. Treacy, K. H. Randall, S. Rao, J. A. Perry, D. J. Chadi, *Z. Kristallogr.* **1997**, *212*, 768.
[51] It has turned out that in many situtations the most efficient way of optimizing the chemical composition actually consists of repeating the global optimization for many different compositions, but keeping the stoichiometry fixed for each individual run.
[52] As a consequence, the number of "atoms" one would get by summing all the corners of the individual polyhedra does not agree with the total number of atoms in the "atom-based" configurations—only after the full structural graph has been generated, is one permitted to identify the remaining corners of the polyhedra with real atoms.
[53] S. Girard, P. Pullumbi, C. Mellot-Draznieks, G. Férey, *Stud. Surf. Sci. Catal.* **2001**, *135*, 254.
[54] This method has been already envisioned by J. V. Smith in 1988 at an early stage in the development of structure prediction tools:[45] "*At the current state of mathematical knowledge, the only successful systematic way to classify known 3-D structures and invent new ones is to look for common sub-units, to find whether such sub-units can be linked together in new ways, and to investigate if the sub-unit can be modified. Still pending is an attempt to build all possible topologies by a systematic search in 3-D space …*".
[55] Usually, the full compound includes additional counter-ions that are needed to fill the cavities in the polyhedra network generated by the AASBU. Thus we speak of the geometry of the "backbone" of the full structure.
[56] J. C. Schön, M. Jansen in *Inorganic Chemistry Highlights* (Eds.: G. Meyer, D. Naumann, L. Wesemann), Wiley-VCH, Weinheim **2002**.
[57] V. R. Saunders, R. Dovesi, C. Roetti, M. Causà, N. M. Harrison, R. Orlando, C. M. Zicovich-Wilson, CRYSTAL98, Torino (Italy), **1998**.
[58] A. S. Averyaqnov, Y. G. Khait, Y. V. Puzanov, *J. Mol. Struct. (THEOCHEM)* **1996**, *367*, 87 and references therein.
[59] So far, for none of these structures a known analogue in a different chemical system has been identified.
[60] Due to the fact that the experimental structures have site occupation factors different from one, they need to be treated as "defect" structures from the modelling point of view. Thus, they do not appear when using standard landscape exploration methods for which statistical occupation is not permitted.
[61] Among these, we would also expect variants of the Li_4CO_4-**I** structure with larger unit cells, which can be constructed by using the unit cell of Li_4CO_4-**I** as a basic building block that is rotated and translated, such as in for example a filled variant of the K_4Ge_4 structure[62] (Li in K and O in Ge positions, respectively, with filled Ge_4 tetrahedra). However, since this structure requires more atoms than we employed in the simulation cell during global optimizations, we did not include it in the analysis presented here.
[62] R. Nesper, *Prog. Solid State Chem.* **1990**, *20*, 1
[63] G. Férey, *C. R. Acad. Sci. Ser. IIc* **1998**, *1*, 1 and references therein.
[64] *Atlas of Zeolite Structure Types* (Eds.: W. M. Meier, D. H. Olson, C. Baerlocher) Elsevier, London, **1996** (update on http://www.iza-sc.ethz.ch/IZA-SC).
[65] J. D. Gale, *J. Chem. Soc. Farad. Trans.* **1997**, *93*, 629.
[66] J. A. Tossell, *J. Phys. Chem.* **1996**, *100*, 14828.
[67] A. R. George, C. R. A. Catlow, *Zeolites* **1997**, *18*, 67.
[68] F. Taulelle, J.-M. Poblet, G. Férey, M. Bénard, *J. Am. Chem. Soc.* **2001**, *123*, 111.
[69] M. Estermann, L. B. Mc Cusker, C. Baerlocher, A. Merrouche, H. Kessler, *Nature* **1991**, *352*, 320.

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