From Octahedral to Icosahedral Metal–Organic Polyhedra Assembled from Two Types of Polyoxovanadate Clusters

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Abstract: Design and synthesis of metal–organic polyhedra (MOPs) with targeted geometries from predetermined secondary building units (SBUs) is a long-standing challenge in chemistry and material science. Theoretical prediction shows that there are 6 possible polyhedra from the 3-coordinated, 4-coordinated octahedron (3,4-c octahedron) to (3,5)-c icosahedron with minimal transitivity (simplest possible). Except for one missing polyhedron (mtr) due to the unfavorable angles, we report five MOPs based on these structures, including an octahedral (3,4)-c VMOP-21 (rdo), an icosahedral (3,5)-c VMOP-25 (troc), and three intermediate derived trinodal (3,4,5)-c VMOP-22–24 (ghm, hmg, xum). Remarkably, all these MOPs obey the minimal transitivity principle and are consistent with geometrical predictions.

Predictable synthesis of crystal structures has been a longstanding challenge in crystal engineering.[1] Part of this challenge can be attributed to the absence of reliable building blocks in which essential information is encoded to give a particular preconceived structure. Reticular chemistry, concerned with the design and synthesis of compounds formed by linking polyatomic secondary building units (SBUs) with chemical bonds,[2] provides a logical approach for surmounting this obstacle. The geometrical design principles of reticular chemistry have seen extensive use in recent years to direct the construction of a plethora of metal–organic frameworks (MOFs) with structures usually based on simple nets.[3] Such nets are identified by the three-letter symbol in the Reticular Chemistry Structure Resource (RCSR).[4] If these MOPs obey the minimal transitivity principle (simplest possible) that states the transitivity of the net for a resulting framework is the minimal possible compatible with the starting components.[5]

Apart from frameworks, this approach is also suitable for the assembly of molecular metal–organic polyhedra (MOPs).[6] Nine basic polyhedra having one kind of vertex and one kind of edge, enumerated by O’Keeffe and Yaghi et al.,[6b] are most suitable as targets for synthesis using molecular building blocks. But, apart from that, targeted synthesis of complex polyhedra with multi-vertices is still far behind the level of the most highly developed part of this discipline, that of MOFs. There are two reasons for this state of affairs: First, unlike MOFs, which, because such a substantial number of them have been synthesized, lends themselves to systematizing their structures and developing a conceptual strategy, the relatively meager reports of MOPs makes it difficult to deduce a general basis for their designed construction. Second, instead of extended nets, the pre-designed, unidirectional branching building blocks in MOPs must have a certain curvature so as to form the closed structures, but the lack of such reliable building blocks makes their designed synthesis, if not impossible, fairly difficult. Up to date, it has not been possible to produce a suite of MOPs of given topologies purposefully.

Polyoxovanadate clusters, formed by the strong covalent interaction between vanadium atoms and oxygen atoms, are promising metal SBUs, as demonstrated by earlier work.[7] Our design strategy is employing highly symmetric polyatomic SBUs combined with structural prediction to construct fascinating MOPs. The selected targets are polyhedra with 3-c (3-coordinated), 4-c and/or 5-c vertices. As a result, our first task is to predict possible MOPs from geometrical perspective. Our second task, also the most challenging issue, is to directionally construct these MOPs by selecting SBUs and linkers of the correct geometry—or conversely to show why one of those does not exist in reality.

Herein a suite of theoretically predicted MOPs that obey the minimal transitivity principle have been constructed by design: VMOP-21–25. Of these MOPs, 3-c vertices are constructed from a tritopic (3-c) organic linker (benzene-1,3,5-tricarboxylic acid, H$_3$btc), whereas 4-c and/or 5-c vertices are provided by polyoxovanadate SBUs (Figures 1a,b). The 4-c metal SBU has been used earlier to construct MOPs by Zaworotko’s, Schmitt’s and our group.[7a–e] However, even though pentagonal moieties exist in inorganic clusters, such as [Mo$_5$O$_{15}$] reported by Müller,[8] the pentagonal 5-c SBU had been missing until we used a [WV$_5$] core of 5-fold symmetry.[9] In addition, the double SBUs (4-c and 5-c SBUs) are found in one MOP for the first time.

In MOFs and MOPs, a key group of materials is that based one metal SBU and one linker. With a polytopic linker the
underlying net will ideally be one with two nodes (binodal) and one kind of link—that is, minimal transitivity $2 \rightarrow 1$. Structures of this type have been reviewed. A key observation is that for polyhedral structures there are only two such structures: an octahedral $(3,4)$-c, symbol $rdo$ and an icosahedral $(3,5)$-c, symbol $trc$. The end members of our suite of structures are indeed based on the two frameworks and so we describe them first.

VMOP-21, $(\text{NH}_2\text{Me}_2)_2[(V_5\text{O}_9\text{Cl})(\text{btc})_6]$, was prepared from VOSO$_4\cdot x$H$_2$O and btc under solvothermal conditions with high yield (see Supporting Information for detailed synthesis). Interestingly, it is essentially the same as an earlier reported by Zaworotko and co-workers, but the cell parameters and stacking patterns are different (Figure S1). The 4-c SBU (Figure 1a) consists of a central [VO$_5$] square pyramid sharing the square edges with four other [VO$_5$] square pyramids. The stoichiometry, including the linked carboxylate groups, is $[V_5\text{O}_9\text{Cl}(\text{CO}_2)_4]^2$ (Table S1). VMOP-21 is an anionic MOP with the dimension of $24 \times 24 \times 24$ Å$^3$ (Figure S2a), twelve dimethylamine cations (H$_2$NMe$_2$)$^+$ were added for charge balance. In contrast to the earlier report, the molecule of VMOP-21 has full cubic symmetry ($m3m = O_h$) and the molecules are arranged as in cubic closest packing with 21 Å between centers (Figure S3a).

When NaVO$_4$ was added in the reaction system, VMOP-25 with formula $(\text{NH}_2\text{Me}_2)_{12}[V_6\text{O}_{11}(\text{SO}_4)(\text{CO}_2)_5]$ was obtained (see Supporting Information for details). The dimension of each molecule is about $29 \times 29 \times 29$ Å$^3$ (Figure S2f). The pentagonal $[V_6\text{O}_{11}(\text{SO}_4)(\text{CO}_2)_5]$ SBU (Figure 1b) has a central [VO$_5$] pentagonal pyramid sharing the pentagon edges with five [VO$_5$] square pyramids. The overall composition, including the linked carboxylates is $[V_6\text{O}_{11}(\text{SO}_4)(\text{CO}_2)_5]$ (Table S1). The molecule has close to icosahedral symmetry (actually $D_3d$) with one molecule in the

![Figure 1](image1.png)

**Figure 1.** a) Octahedral $(3,4)$-c $rdo$ MOP based on tetragonal $[V_5\text{O}_9\text{Cl}(\text{CO}_2)_4]$ SBUs and btc ligands. b) Icosahedral $(3,5)$-c $trc$ MOP based on pentagonal $[V_6\text{O}_{11}(\text{SO}_4)(\text{CO}_2)_5]$ SBUs and btc ligands. c) The crystal structure of icosahedral VMOP-25 constructed from 12 pentagonal SBUs and 20 btc ligands.

![Figure 2](image2.png)

**Figure 2.** a) The convex deltahedra with 4-c (red ball) and/or 5-c vertices (blue ball), the numbers on the top indicate the respective numbers of 4-c and 5-c vertices. b) The corresponding $(3,4,5)$-c polyhedral nets when 3-c vertices (green ball) are added in the center of each face, where $rdo$ has only 3-c and 4-c vertices (red ball) and $trc$ has 3-c and 5-c vertices (blue ball). c) 3-c vertices in different polyhedra link with different ratios of 4-c (red square) and 5-c vertices (blue pentagon), $rdo$ with only 3-c and 4-c vertices and $trc$ with only 3-c and 5-c vertices. **ghm**, **hmg**, and **xum** with two distinct 3-c vertices link with different ratios of 4-c and 5-c vertices.
primitive cell and arranged again in cubic closest packing, now with a spacing of 31–32 Å between molecules (Figure S3c). Each nanocage is composed of 636 atoms including 12 \([\text{V}_6\text{O}_{11}(\text{SO}_4)(\text{CO}_2)_5]\) SBUs and 20 btc ligands. The structure is illustrated in Figure 1c. Other than carboranes and fullerenes there has been only very few reports of icosahedral molecules. Some reported molecules with icosahedral symmetry are very different from a MOP as they all have purely inorganic frameworks (see Figure S4 in the Supporting Information).\(^{[11]}\) Only two types of MOPs with icosahedral topology have been documented (Figure S5),\(^{[12]}\) however, their common feature is both through self-assembly, rather than by directed assembly.

We now ask, what are the possibilities for \((3,4,5)\)-c polyhedra with just one kind of 4-c and one kind of 5-c vertex?\(^{[13]}\) The answer comes from consideration of the convex deltahedra (a deltahedron is a polyhedron with equilateral triangular faces). These are well known in chemistry as, for example, the frameworks of the closo-carboranes. The six predicted polyhedra with 4-c and/or 5-c vertices are shown in Figure 2a. They range from the octahedron with six 4-c vertices to the icosahedron with twelve 5-c vertices. There are four intermediates with 7, 8, 9, and 10 vertices—they have just one kind of 4-c and one kind of 5-c vertex (the minimum possible). To derive \((3,4,5)\)-c polyhedra, a 3-c vertex should be placed in each face as shown in Figure 2b. In the real molecules the 3-c vertex must be planar so that is consistent with conformation chosen for our derived polyhedra.

We note that the polyhedron, \textit{mtr}, derived from the 7-vertex deltahedron is the only one with one kind of 3-c vertex. Unfortunately, as can be seen from Table S2, this geometry requires very unfavorable acute angles at the 4-c vertices and is in fact the only structure we have been unable to realize in a MOP. In the database of RCSR, there is another \((3,4,5)\)-c polyhedron, \textit{mts}\(^{[11]}\) but this is also unfavorable as it requires the 4-c and 5-c vertices to be almost planar (Table S2 and Figure S6). The other three polyhedra, 8-vertex \textit{ghm}, 9-vertex \textit{hmg}, and 10-vertex \textit{xum}, require two distinct 3-c vertices to link with different ratios of 4-c and 5-c vertices, so the minimal number of vertices is four as found (Figure 2c).

These predicted polyhedra have all been realized (but notably no others) as now described. Three intermediate derived polyhedra, VMOP-22 to VMOP-24, were synthesized under similar conditions with small variations (see Supporting Information for detailed synthesis). The crystal structures of VMOP-22 to VMOP-24 are shown in Figure 3a, the dimensions of these MOPs are \(25 \times 21 \times 21 \text{ Å}^3, 26 \times 26 \times 18 \text{ Å}^3\) and \(33 \times 22 \times 22 \text{ Å}^3\), individually (Figures S2b–e). The pentagonal \([\text{MoV}_5]\) SBU in VMOP-22 and 23 has the same geometry with \([\text{V}_6]\) SBU in VMOP-25 (Table S1), while the geometry of \([\text{V}_6]\) SBU in VMOP-24 is a bit distorted. The molecule of each VMOP has different symmetry and the molecules are arranged in different distance of closest packing in primitive

\begin{figure}
  \centering
  \includegraphics{figure3}
  \caption{a) The real molecules structures of VMOP-21–25 established by X-ray crystallography.\(^{[16]}\) H atoms have been omitted for clarity. There are two types of polyoxovanadate SBUs, tetragonal \([\text{V}_4]\) SBUs (marked in red) and pentagonal \([\text{MV}_5]\) SBUs (marked in blue, \(M = \text{Mo} \) or \(V\)). b) The augmented (truncated) forms of \textit{rdo}, \textit{ghm}, \textit{hmg}, \textit{xum}, and \textit{trc} symbolizes as \textit{rdo-a}, \textit{ghm-a}, \textit{hmg-a}, \textit{xum-a}, and \textit{trc-a}. The blue pentagonal, red quadrangular and green triangular planar geometry are evolved from \([\text{V}_4]\) SBUs, \([\text{MV}_5]\) SBUs and btc ligands. c) Polyhedral models of VMOPs are represent as \textit{rdo-e}, \textit{ghm-e}, \textit{hmg-e}, \textit{xum-e}, and \textit{trc-e}, in which the carbon atoms in carboxylate groups of the BTC ligands are chosen as vertices of polyhedra, carboxylate-based SBUs \([\{\text{MV}_5(\text{CO}_2)_{5}\}\], \([\{\text{V}_5(\text{CO}_2)_{4}\}\]), and btc ligands can act as faces of a pentagon, a tetragon and a trigon, respectively.}
\end{figure}
cells (Figures S3b–d). Unlike VMOP-21 and VMOP-25, the common feature of the three other MOPs is that they are all (3,4,5)-c polyhedra, in which 3-c vertex is btc ligand, 4-c vertex is V, SBU and 5-c vertex is MV, SBU (M = Mo or V). The components are (3-c),(4-c),(5-c), (VMOP-22, ghm), (3-c),(4-c),(5-c)h (VMOP-23, hmg) and (3-c),(4-c),(5-c)h (VMOP-24, xum), respectively (Table S3). The number of 4-c and 5-c vertices of these polyhedra has a regular change rule: with the number of 4-c vertex is reduced by one, corresponding two 3-c and two 5-c vertices will be added in order to maintain the polyhedral geometries. The augmented nets (ghm-a, hmg-a and xum-a) of VMOP-22 to 24 are shown in Figure 3b, in which the trigon is btc ligand, tetragon is V, SBU and pentagon is MV, SBU. To obtain a better understanding of their polyhedral geometries, the edge nets of VMOP-22 to 24 (ghm-e, hmg-e and xum-e) are simplified by using the carboxylic carbon atoms of btc as new vertices (Figure 3c). To our knowledge, these derived convex polyhedra (VMOP-22 ghme with 38 faces; VMOP-23 hmg-e with 44 faces; VMOP-24 xum-e with 50 faces) are first discovered in the field of polyhedra. Meanwhile, the numbers of faces (F), edges (E) and vertices (V) of these polyhedra obey Euler’s polyhedron formula $V - F + E = 2$. Interestingly, paper models of these polyhedra can be made as shown in Figure S7. These three paper models can provide a means to intuitively estimate the existence of these new polyhedra in geometry. Simple geometric arguments show that the polyhedra of these molecules are the only ones with triangular faces, one kind of 4-c and/or one kind of 5-c vertex. Accordingly, we assert that the found polyhedra are the simplest possible. In VMOP-21 and VMOP-25, there is one kind of metal SBU (called A) and a tritopic linker (called B). There must correspond to just one kind of edge (A–B) and so minimal possible transitivity 2 1 1 (Table S4). In VMOP-22–24, there are two kinds of metal SBUs (A and B) and two kinds of tritopic linkers (C and D). There must be four kinds of edges (A–C, A–D, B–C, and B–D), so transitivity 4 4 4 is minimal (Table S4).[3]

Given that the counterions of these MOPs are dimethylamine cations in these MOPs can be completely exchanged by other metal ions. At the outset of this study, it was believed to be difficult, if not impossible, to achieve the target MOPs by directed synthesis. This report demonstrates that this hurdle can be overcome by combining with predesigned building-block approach, and a sequence of MOPs based on polyoxovanadate SBUs, including an octahedral (3,4)-c VMOP-21 (rd), an icosahedral (3,5)-c VMOP-25 (trc), three intermediate derived trinodal (3,4,5)-c VMOP-22–24 (ghm, hmg, xum), have been constructed by design. All these MOPs have minimal transivities and are consistent with geometrical predictions. The only one theoretically expected but actually unobserved polyhedron (mtr) is not formed owing to the unfavorable angles. Besides, the given polyoxovanadate SBUs with specific geometries and coordination modes, for example, tetragonal V and pentagonal V, and MoV, SBU, provide reliable building blocks for target synthesis of specific MOPs. Last but not least, in view of the advances in reticular...
chemistry and in the assembly of large-cage molecules, our work is at the well-placed at the confluence of these two subjects and may thereby further improve our ability to make molecules at will.

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** cation exchange · metal-organic polyhedra (MOPs) · minimal transitivity · polyoxovanadate · reticular chemistry


[16] CCDC 1836310, 1831335, 1831336, 1831337, 1838490, and 1866623 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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From Octahedral to Icosahedral Metal–Organic Polyhedra Assembled from Two Types of Polyoxovanadate Clusters

Hol den MOP: Mithilfe des Konzepts der retikulären Chemie werden metallorganische Polyeder (MOP) entwickelt. Theoretische Berechnungen und experimentelle Charakterisierungen zeigen eine Reihe von dreifach, vierfach und fünffach koordinierte MOPs, die auf Polyoxovanadat-Bausteinen aufbauen und alle dem Prinzip der minimalen Transitivität gehorchen.