New Directions in Polyvanadate Chemistry: From Cages and Clusters to Baskets, Belts, Bowls, and Barrels

By Walter G. Klemperer,* Todd A. Marquart, and Omar M. Yaghi

Like other early transition-metal polyoxoanions, large polyvanadates are known to adopt complex cage/cluster structures.1 The Keggin structure observed in the anion of 123 is typical. Here, the \([\text{V}_12\text{O}_{38}]^{6-}\) cage A\(^{[**]}\) encapsulates a \(\text{PO}_{4}^{3-}\) anion. This cage is defined by 24 bridging oxygen atoms, and 14 of its 18 square faces are occupied by vanadium atoms, each of which is bonded to a terminal oxygen atom. The closely related Schlemper structure was first observed in 2.3 Here, the \([\text{V}_{16}\text{O}_{44}]^{12-}\) cage B encapsulates a water molecule. This cage is also defined by 24 bridging oxygen atoms, but all 18 of its square faces are occupied by \(\text{V} = \text{O}\) groups. The Keggin and Schlemper structures are very similar since they are both based on \(\text{O}_8\) cage frameworks. They differ in that the 24 bridging oxygens define the vertices of the \(\text{O}_8\) rhombicuboctahedron in Keggin structures and the \(\text{D}_8\) elongated square gyrobicupola in Schlemper structures.4

Research in polyvanadate chemistry has very recently expanded beyond classical cage/cluster structures to include hitherto unknown basket, belt, bowl, and barrel structures shown in C–H. The \([\text{V}_{16}\text{O}_{44}]^{12-}\) basket C contains an acetonitrile molecule in crystalline 3.4 The belt-shaped \([\text{V}_{8}\text{O}_{24}]^{6-}\) anion D is found in 4,5 where it encircles an oxalate ion. Two vanadate bowl structures are also shown: One (E) is observed in 5,6 where the \([\text{V}_{4}\text{O}_{12}]^{12-}\) bowl contains a nitrate ion, and in 6,7 where the \([\text{V}_{4}\text{O}_{12}]^{12-}\) ion contains a potassium ion. The second, the \([\text{V}_{8}\text{O}_{24}]^{6-}\) bowl F, contains a \(\text{Cl}^{-}\) ion in 7.8 In 8, \([\text{V}_{8}\text{O}_{24}]^{6-}\) units G are joined together by \(\text{CH}_3\text{P}^4+\) groups to form \([\text{CH}_3\text{P}_4]_8\text{V}_{16}\text{O}_{56}^{14-}\) barrels H that contain tetramethylammonium cations.

These recent developments in polyvanadate chemistry raise interesting questions regarding structural principles. Clearly, the new structures C–F can be viewed as fragments of classical Keggin and Schlemper cages A and B, but what about the barrel fragment G or the recently reported \([\text{V}_{20}\text{O}_{56}]^{10-}\)9,10 \([\text{V}_{22}\text{O}_{56}]^{12-}\)10 and \([\text{V}_{18}\text{O}_{44}]^{6-}\) cages in 9, 10, and 11? What about larger cages that are yet to be

\[\text{K}_{12}[\text{V}_{20}\text{O}_{56}]:20\text{H}_2\text{O} 9\]
\[(\text{NEt}_4)_4[\text{H}_2\text{V}_{22}\text{O}_{56}(\text{ClO}_4)] 10\]
\[(\text{NEt}_4)_4[\text{H}_2\text{V}_{20}\text{O}_{44}(\text{N}_3)] 11\]

\[\text{PPh}_4][\text{MeCN} – (\text{V}_{2}\text{O}_{32})] 3\]
\[(\text{NBu}_4)_2[\text{V}_{4}\text{O}_{12}(\text{OEt})_{12}(\text{C}_2\text{O}_4)] 4\]
discovered? An answer to these questions is to be found in the infinite sheet (Fig. 1) observed in the V₂O₅ layer structure.¹¹¹ Consider first the \([\text{V}_2\text{O}_5]^\text{13-}\) bowl structure E. When flattened out into a sheet, this structure becomes the fragment of the V₂O₅ sheet labeled in orange (Fig. 1) after terminal oxygen atoms have been removed. The barrel fragment G is similarly displayed as the green V₂O₅ sheet fragment. In other cases, structures can be flattened into V₂O₅ sheet fragments, fold them up, and stitch them together to generate new polyvanadate structures. The recently discovered metastable \(\gamma\)-V₂O₅ polymorph¹² can be derived from the V₂O₅ structure in an analogous fashion by first removing the terminal oxygen atoms, then corrugating the infinite sheet structure, and finally reintroducing the terminal oxygen atoms in new positions.

![Diagram of V₂O₅ sheet structures](image)

The relationship between V₂O₅ sheets and polyvanadate baskets, belts, bowls, and barrels extends beyond topology into chemistry. The sheets of VO₅ square pyramids found in V₂O₅ and related vanadates such as \(\alpha\)-VOPO₄¹³ are bonded together by weak V–O bonds, 2.8 Å long. As a result, the layers are easily separated to form intercalation complexes.¹¹¹,¹⁴ In classical vanadate cages, a similar structural situation is observed. The cage of VO₅ square pyramids in the anion of \(\mathbf{2}^{[3]}\) for example, is bonded to an encapsulated water molecule by very weak V–O bonds. “Intercalation” chemistry is impossible, however, since the cage framework blocks access to the vanadium coordination sites. Such is not the case with the new structures C–F and H, where access to square-pyramidal vanadium centers is relatively unrestricted, and guest–host chemistry becomes a real possibility. To date, only the \([L = (V_{12}O_{22})]\) system has been investigated from this point of view,¹⁴,¹⁵ but a rich chemistry can be anticipated given the analogy with the solid oxide guest–host chemistry of zeolites.

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