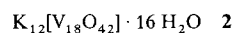
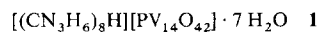


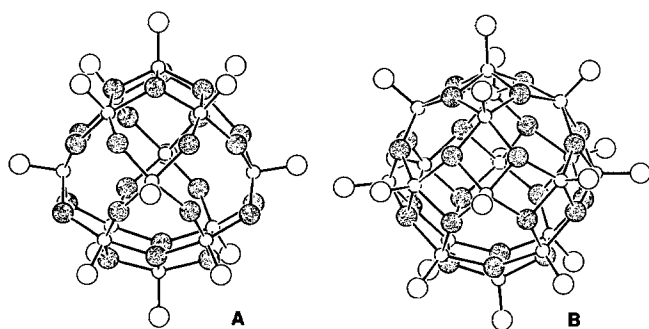
New Directions in Polyvanadate Chemistry: From Cages and Clusters to Baskets, Belts, Bowls, and Barrels

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

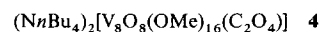
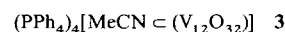
Like other early transition-metal polyoxoanions, large polyvanadates are known to adopt complex cage/cluster structures.^[1] The Keggin structure observed in the anion of **1**^[2] is typical. Here, the $[V_{14}O_{38}]^{6-}$ cage **A**^[**] encapsulates



a 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 $[V_{18}O_{42}]^{12-}$ 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 V=O groups. The Keggin and Schlemper structures are very similar since they are both based on O_{24} cage frameworks. They differ in that the 24 bridging oxygens define the vertices of the O_h rhombicuboctahedron in Keggin structures and the D_{4d} elongated square gyrobicupola in Schlemper structures.^[4]



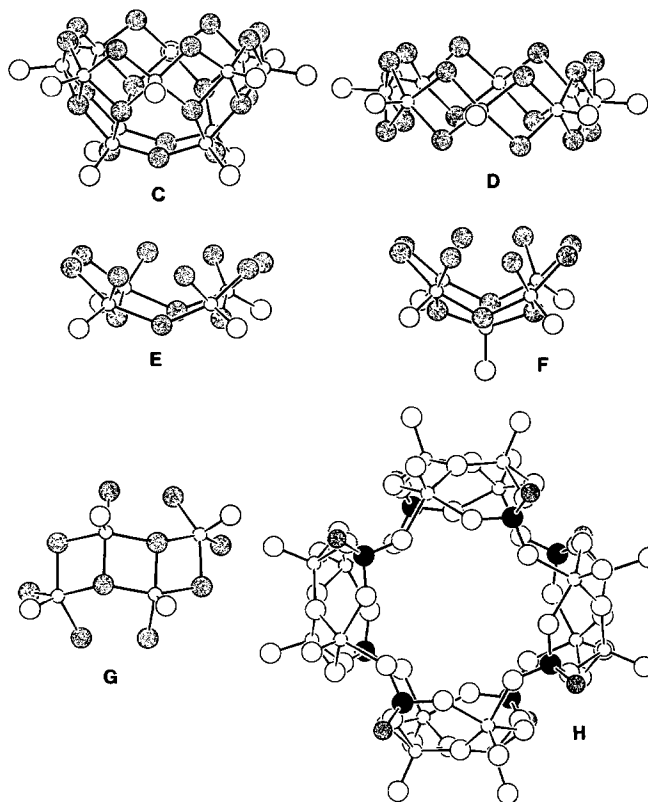
Research in polyvanadate chemistry has very recently expanded beyond classical cage/cluster structures to include hitherto unknown basket, belt, bowl, and barrel structures shown in **C–H**. The $[V_{12}O_{32}]^{4-}$ basket **C** contains an acetonitrile molecule in crystalline **3**.^[4] The belt-shaped $[V_8O_{24}]^{16-}$ anion **D** is found in **4**,^[5] where it encircles an



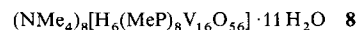
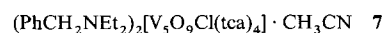
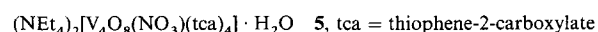
[*] Prof. W. G. Klemperer, T. A. Marquart, O. M. Yaghi
Department of Chemistry and
Beckman Institute for Advanced Science and Technology
University of Illinois
Urbana, IL 61801 (USA)

[**] In structures **A–G** bridging oxygens are represented by large shaded spheres, terminal oxygens by large open spheres, and vanadium atoms by small open spheres. For the sake of clarity, the CH_3P^{4+} groups in **H** are shaded, and vanadium and oxygen atoms are represented by small and large open spheres, respectively. In the structures **I–L** the vanadium atoms are represented by small black spheres and oxygen atoms by large open spheres.

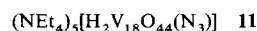
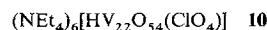
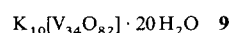
oxalate ion. Two vanadate bowl structures are also shown: One (**E**) is observed in **5**,^[6] where the $[V_4O_{16}]^{13-}$ bowl contains a nitrate ion, and in **6**,^[7] where the $[V_4O_{16}]^{12-}$ ion contains a potassium ion. The second, the $[V_5O_{17}]^{13-}$ bowl **F**, contains a Cl^- ion in **7**.^[6] In **8**, $V_4O_{14}^{11-/12-}$ units **G** are joined together by CH_3P^{4+} groups to form



$[(CH_3P)_8V_{16}O_{56}]^{14-}$ 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 $[V_{30}O_{74}]^{10-}$,^[9] $[V_{22}O_{54}]^{6-}$,^[10] and $[V_{18}O_{44}]^{6-}$ ^[10] cages in **9**, **10**, and **11**? What about larger cages that are yet to be



discovered? An answer to these questions is to be found in the infinite sheet (Fig. 1) observed in the V_2O_5 layer structure.^[11] Consider first the $[V_4O_{16}]^{13-}$ bowl structure **E**. When flattened out into a sheet, this structure becomes the fragment of the V_2O_5 sheet labeled in orange (Fig. 1) after terminal oxygen atoms have been removed. The barrel fragment **G** is similarly displayed as the green V_2O_5 sheet fragment. In other cases, structures can be flattened into V_2O_5

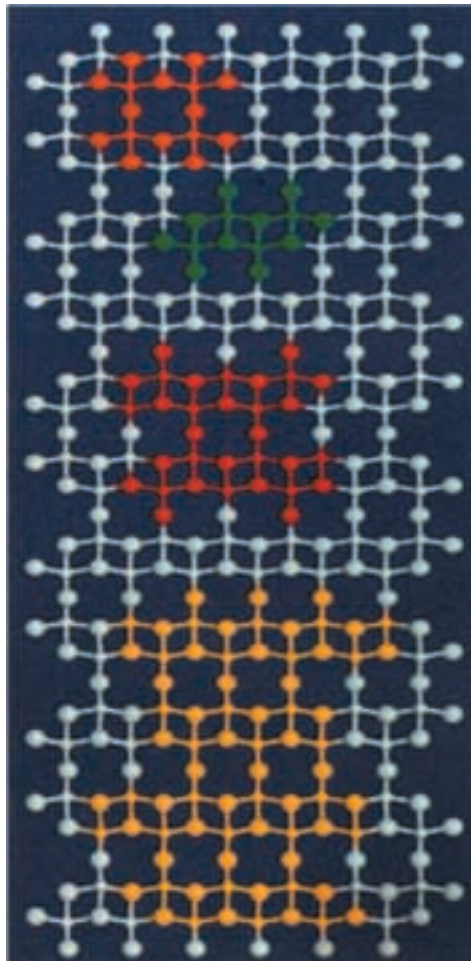
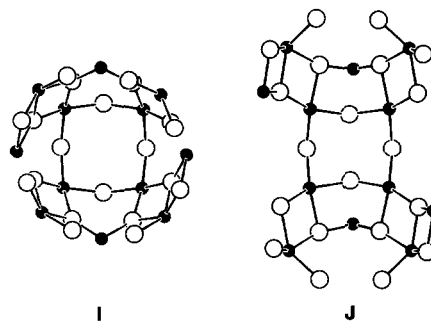
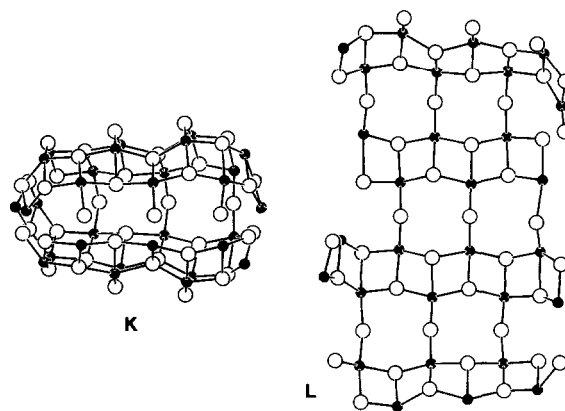


Fig. 1. Fragment of the V_2O_5 layer structure (small spheres represent vanadium; large spheres oxygen; for clarity the terminal oxygen atoms at the square-pyramidal vanadium centers have been omitted). The colored V–O units are observed in new, molecular polyvanadate structures. For details, see text.

sheet fragments only after cleaving selected V–O bonds. In the $[V_{12}O_{32}]^{4-}$ basket, for example, eight V–O bonds must be cleaved as in **I**, where terminal oxygen atoms have been omitted for clarity. Only then can the basket be flattened (see **J**) into the red V_2O_5 fragment of Figure 1. Large cage structures can be reduced to V_2O_5 layer fragments in the same way. The $[V_{30}O_{74}]^{10-}$ cage in **9**^[9] is reduced to the yellow V_2O_5 fragment at the bottom of Figure 1 after cleaving 15 V–O bonds, as shown in **K** and **L**. The $[V_{22}O_{54}]^{6-}$ (**10**^[10]) and $[V_{18}O_{44}]^{6-}$ (**11**^[11]) cages both reduce to V_2O_5 fragments that are subfragments of this yellow fragment after 14 bonds are broken. The purpose of the exercise is now clear: by reversing the procedure, it is possible to cut out

V_2O_5 sheet fragments, fold them up, and stitch them together to generate new polyvanadate structures. The recently discovered metastable γ' - V_2O_5 polymorph^[12] can be derived from the V_2O_5 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.



The relationship between V_2O_5 sheets and polyvanadate baskets, belts, bowls, and barrels extends beyond topology into chemistry. The sheets of VO_5 square pyramids found in V_2O_5 and related vanadates such as α - $VOPO_4$ ^[13] are bonded together by weak V–O bonds, 2.8 Å long. As a result, the layers are easily separated to form intercalation complexes.^[11, 14] In classical vanadate cages, a similar structural situation is observed. The cage of VO_5 square pyramids in the anion of **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 $[L \subset (V_{12}O_{32}^{4-})]$ system has been investigated from this point of view,^[4, 15] but a rich chemistry can be anticipated given the analogy with the solid oxide guest–host chemistry of zeolites.

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