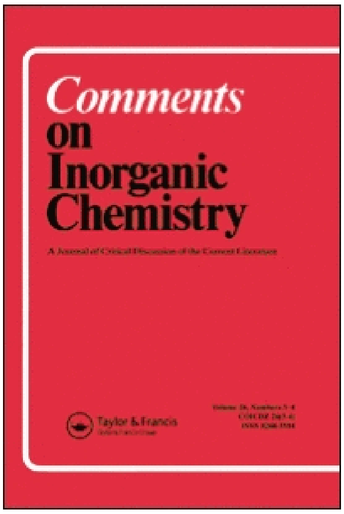


Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Clusters and Solid Phases of the Oxovanadium-Phosphate and -Organophosphonate Systems

Jon Zubieta[a]
[a] Department of Chemistry, Syracuse University, Syracuse, New York

To cite this Article Zubieta, Jon(1994) 'Clusters and Solid Phases of the Oxovanadium-Phosphate and -Organophosphonate Systems', Comments on Inorganic Chemistry, 16: 3, 153 — 183
To link to this Article: DOI: 10.1080/02603599408035857
URL: http://dx.doi.org/10.1080/02603599408035857

Clusters and Solid Phases of the Oxovanadium–Phosphate and –Organophosphonate Systems

JON ZUBIETA
Department of Chemistry,
Syracuse University,
Syracuse, New York 13244

Received February 2, 1994

A major challenge facing the synthetic inorganic chemist is the synthesis of solid materials with specifically designed properties. However, small soluble molecular building blocks with well-defined reaction chemistries which would allow low-temperature assembly into crystalline solid state inorganic materials are not well known. Low temperature strategies which show some promise for the rational design of solids include solvothermal reactions, consensation/hydrolysis, and the introduction of templates or guest molecules for the organization of more complex structures. By exploiting these techniques, the rich structural chemistries of the V/O/PO_4^{3-} and related organically derivatized V/O/RPO_3^{2-} systems with a variety of organic and inorganic templates have begun to emerge. Several features of this chemistry are outlined.

Key Words: *oxovanadium phosphate phases, oxovanadium organophosphonate clusters and phases, layered solids, open framework solids*

INTRODUCTION

The metal oxo-unit {M═O} is a fundamental consituent both of "simple" soluble clusters and of complex solid materials. The sorp-

Comments Inorg. Chem.
1994, Vol. 16, No. 3, pp. 153–183
Reprints available directly from the publisher
Photocopying permitted by license only

tive and catalytic properties associated with metal oxide phases of various compositions are of central importance to the global production of useful chemicals. The soluble clusters serve not only as model systems which provide insights into the fundamental nature of the solid systems and potential synthetic precursors for their design, but as materials which exhibit useful catalytic and sorptive properties of their own. This review is concerned with the synthesis of metal oxide clusters which serve as models and as potential molecular building blocks for new solid materials or supramolecular assemblies and with the direct synthesis by hydrothermal techniques of complex solid materials from simple inorganic and organic precursors.

One approach to increase the selectivity of chemical reactions is to control the type and geometric location of atoms in the immediate environment of the reactive site. While enzymes are the most readily appreciated examples of "molecular recognition" by control of local geometry, strong size and shape selectivites are inherent in many zeolitic solids.[1,2] However, these silicoaluminates and aluminophosphates possess closed shell electronic structures which makes them ineffective for atom abstraction and redox reactions, which are characteristic of d-block elements and of solid metal oxides.

In order to exploit the size selectivity of the zeolites and the reactivity of transition elements, the target material should combine the microporous property of molecular-sized cavities, the thermal and chemical stability of a metal oxide, and the presence of transition metal cations. The preparation and characterization of such designer solids represents an emergent theme of the inorganic chemical literature.[3,4]

A number of chemical and physical characteristics are of importance in designing such solids. These include crystallinity to achieve a high degree of absorption specificity, a reasonable degree of chemical and thermal stability, and a high dimensionality pore structure with a high degree of connectivity to ensure sorption of guest molecules. Furthermore, the transition metal site should display actual or incipient coordinative unsaturation for activity and must physically communicate with the cavity available for guest absorption.[5]

The chemical constituents required for the design of a solid state material possessing such characteristics include transition metal centers, anionic multidentate and/or ambidentate oxo-ligands, and a readily removed templating agent. A transition element is essential to the framework since the desired applications of the solid include oxidation/reduction, free-radical chemistry or atom abstraction reactions, all of which are facilitated by transition elements. Metal oxo-ligation, either as terminal M=O groups or bridging M–O–M units, may also be a desirable feature, since the formation of M–O–M bonds facilitates the assembly of the three dimensional framework of the solid. Furthermore, oxides are characterized by thermal stability and are both ubiquitous components of matter on the Earth's crust and the most versatile of industrial heterogeneous catalysts.[6] An oxoanion component, such as silicate or phosphate, would endow the compostion with mechanical, chemical and thermal stability. The high negative charge of the oxoanions favors the formation of anionic frameworks, a feature of some importance since the most practical route to microporous materials exploits the removal of a cationic template from an anionic framework.

The recent demonstration of the varied solid state chemistry of the molybdenum phosphate system,[5,7–12] the extensive use of phosphate units in the preparation of numerous new materials,[13] and the extensive chemistry of the metal–organophosphonate systems[14–33] suggest that phosphate and/or organophosphonates would provide appropriate anionic components for the preparation of three dimensional networks of corner- and edge-sharing metal polyhedra and anion tetrahedra capable of encapsulating removable cations. The choice of vanadium as the metal component rests on the catalytic relevance of the V/P/O system.[34,35] Vanadylphosphates, $[VOPO_4]$[36] and α-$[VOPO_4]\cdot 2H_2O$[34] are lamellar compounds which undergo intercalation reactions with species as diverse as alcohols,[37c] pyridine,[37e] amides,[37f] metal ions,[37g,37h] quaternary ammonium salts[37i] and ferrocene.[37j] The related layered solid pyrophosphate $[(VO)_2P_2O_7]$ is effective in the catalytic air oxidation of butane to maleic anhydride.[37] The interlayer spaces of these lamellar solids provide reaction vessels of molecular dimensions in which the organic substrate is held in the proper orientation for a specific chemical reaction.[3] The related vanadium organophosphonates belong to a class of layered solid compounds with alternating inorganic layers. Such compounds exhibit sorptive and catalytic properties and serve as models for organic/inorganic interfaces. Vanadyl organophosphonates intercalate alcohols by coordination of the intercalating molecule between the inorganic vanadium phosphate layer.[38] Furthermore, the introduction of other cations to produce ternary compositions of the $M^{n+}/V^{m+}-P-O$ system allows a dramatic expansion of the structural chemistry of these phases, giving a variety of lamellar and channel structures with the cations located in the interlamellar regions or occupying the hydrophilic channels.[39–43] The structural types adopted by these reflect not only the identity of the cation M^{n+} but the vanadium oxidation state, the pH of the solution and consequently the degree of protonation of the phosphate residues $(H_nPO_4)^{(3-n)-}$ ($n = 0$, 1, or 2), and the presence of aquo coligands.

In view of these considerations, the V/O/phosphate and the V/O/organophosphonate systems possess chemical and structural characteristics which may be exploited in the preparation of solid materials with lamellar and/or tunnel structures. In combination with appropriate removable templates, such solids may provide precursors or at the very least primitive models for microporous materials with sorptive and/or catalytic properties.

SYNTHETIC STRATEGIES

The ability to synthesize solid materials according to rational designs is still somewhat primitive. Solid state reactions are most often carried out under conditions where only the most stable products are obtained, and the solid state analogue of organic functional group chemistry is only now beginning to emerge. At the temperatures of most solid state reactions, there is little hope of accomplishing the assembly of a compound of predictable structure from two or more pieces, while retaining the bond relations between most of the constituent atoms.

However, several low temperature strategies are available for the synthesis of solid materials. A wide variety of metastable materials may be prepared by exploiting the techniques of "chimie douce" or "soft chemistry," which employs temperatures ranging from ambient to 300°C.[44–46] Hydrothermal synthesis and hydrolysis/condensation reactions are the specific techniques of "chimie douce" which we have sought to exploit in our investigations.

Hydrothermal syntheses are conventionally carried out in water at 150°C to 250°C at autogenous pressure. The lower viscosity of water under these conditions results in enhanced rates of solvent extraction of solids and crystal growth from solution.[47] Since differential solubility problems are minimized, a variety of synthetic precursors may be introduced. An additional advantage is that a variety of templating cations, including organic cations, may be employed, and, during the crystallization process, the templates of appropriate size or geometry to fill the crystal vacancies are "selected" from the mixture. The technique exploits the principle of "self-assembly" of the metastable solid phase from soluble precursors at relatively low temperatures.

Another potential route to designer materials relies on "fragment condensation" where chemical control of inorganic hydrolysis-condensation reactions may lead to tailor made oligomers or solid polymers. The sol gel processing of glasses and ceramics is the most extensively explored example of this reaction chemistry.[48–50] Under conventional synthetic conditions, molecular species present at the initial stages of the hydrolysis/condensation processes may be isolated, and the structures and properties of these species may be related to those of solid materials formed under more forcing conditions. Furthermore, these molecular species may provide precursors for condensation under mild hydrothermal conditions.

THE VANADIUM–OXO–PHOSPHATE SYSTEM

1. General Considerations

Vanadium phosphorus oxides have a rich and complex chemistry that remains incompletely explored. While these solids may be grossly described as networks of edge- and corner-sharing vanadium polyhedra and phosphorus tetrahedra, the structural variations consistent with this overall motif are quite daunting. The coordination geometries at the V centers are highly variable: tetrahedral (V^V), square pyramidal (V^{IV}, V^V), octahedral (V^{III}, V^{IV}, V^V) and trigonal-bipyramidal (V^{IV}, V^{V}).[51] In addition, the V centers may coordinate to combinations of terminal oxo-groups, bridging oxo-groups, aquo-ligands and phosphate oxygens. The phosphate ligands may be present in a variety of protonation states $\{H_nPO_4\}^{(3-n)-}$ ($n = 0$, 1 and 2) and coordination modes. The hydroxyl groups of $\{H_nPO_4\}$ moieties are invariably unligated to the V centers, thus providing a structural unit for termination of layers or stacks and for reduction of the networking of the (V–O–P) backbone. The phosphate groups may adopt μ_2-bridging modes, coordinating to two dimeric V cores, or may bridge V centers of four independent metal subunits, or may exhibit a combination of bridging and terminal coordination modes. Additional structural variability may be produced by introducing organophosphonate groups $\{RPO_3\}^{2-}$, which also exhibit flexibility of coordination mode. Furthermore, the V/P ratio is variable within at least the 0.5 to 2.0 range.

The structure adopted by the solid is also determined by the templates employed, which may determine whether a lamellar or tunnel structure is adopted and which also produce considerable variations in the volume of the void space and in the details of the geometries and intersections of the channels in these structures. While the use of organic and inorganic templates, generally alkylammonium cations and alkali metal cations, to direct the structural assembly of microporous solids is well established,[44] the templating mechanism is not completely understood. Since both charge-compensation and space-filling effects may contribute to the process, considerable structural variability may be introduced by exploiting different templates. A rich and varied structural chemistry associated with the V/P/O system is emerging, based on the introduction both of inorganic cations and of organic templates.

2. V/O/P Phases Incorporating Inorganic Cations Exclusively

The inorganic phases of the M^{n+}/V/P/O system are represented by one-dimensional, layered and three-dimensional or framework solids, as illustrated in Fig. 1. The structure of $Sr_2[V(PO_4)(HPO_4)_2]$ (**1**) consists of one-dimensional linear chains of corner-sharing $\{VO_6\}$ octahedra bridged by phosphate and hydrogen phosphate tetrahedra.[52,53] The structure illustrates the geometric consequences of introducing highly reduced V(III) sites into V/P/O phases. Vanadium(III) appears to invariably adopt distorted octahedral geometry, rather than the square pyramidal coordination assumed by V(IV) and V(V) centers in these solids. The common layer structure is illustrated by $Rb_{0.5}[VO(PO_4)(H_2O)]$ (**2**), whose structure consists of layers of distorted vanadium octahedra and phosphate tetrahedra with the cations occupying the interlamellar region. The layer is a 4-connected net in which corner-sharing vanadium and phosphorus polyhedra alternate. The coordinated H_2O molecules project into the interlamellar region and form strong interactions with the Rb^+ cations. In contrast to **1**, solid **2** is a mixed valence V(V)/V(IV) species.[54] Framework or three-dimensional solids are represented by the structure of $Cs[(V_2O_3)(HPO_4)_2(H_2O)]$ (**3**), which exhibits the $\{(VO)_2(\mu\text{-}O_2PO_2H)_2\}$ metal core common to many M/P/O phases.[55] Each vanadium octahedron is linked to two adjacent vanadium octahedra through a pair of shared *trans* oxo-groups which assume non-symmetrical bridging modes; this chain of fused octahedra provides the structural motif by expansion of the basic unit along the crystallographic *a* direction. The Cs^+ cations occupy hydrophilic tunnels, into which the pendant –OH groups of the $(HOPO_3)^{2-}$ units also project.

While structures **1–3** exemplify the one-dimensional polymer, two-dimensional layer, and three-dimensional framework structures adopted by M^{n+}/V/P/O phases, extensive structural variability within these general classes of materials may be introduced by modification of reaction conditions or introduction of alternative templating cations. For example, a curious feature of the channel structure adopted by **3** is its gross similarity to that of β-$RbV(HPO_4)_2$ (**4**). While β-$RbV(HPO_4)_2$ is a V(III) species with no terminal V=O bonds or bridging V–O–V units, in contrast to **3**, a V(IV)/V(V) species with both V=O and V–O–V units, both structures provide cation channels formed from edge-sharing of six vanadium octahedra and six phosphorus tetrahedra with four pendant –OH groups projecting into the channel. Furthermore, adjacent channels are linked through a 4-connect domain of two vanadium octahedra and two phosphorus tetrahedra. This observation demonstrates the notable flexibility of extended structures available through the corner-linking of octahedral and tetrahedral units and also suggests that a topological classification of tunnel-

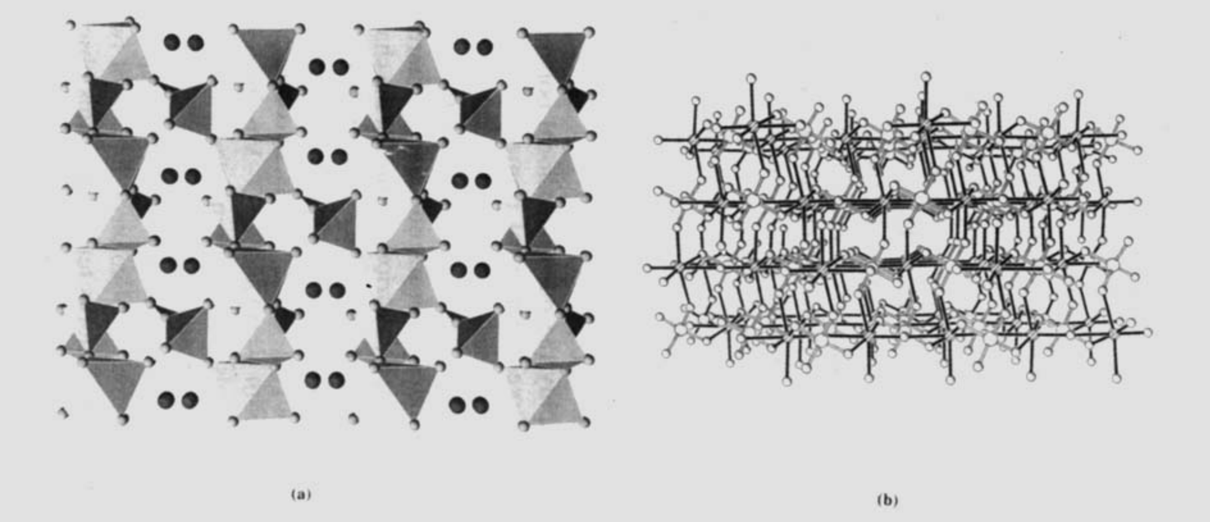
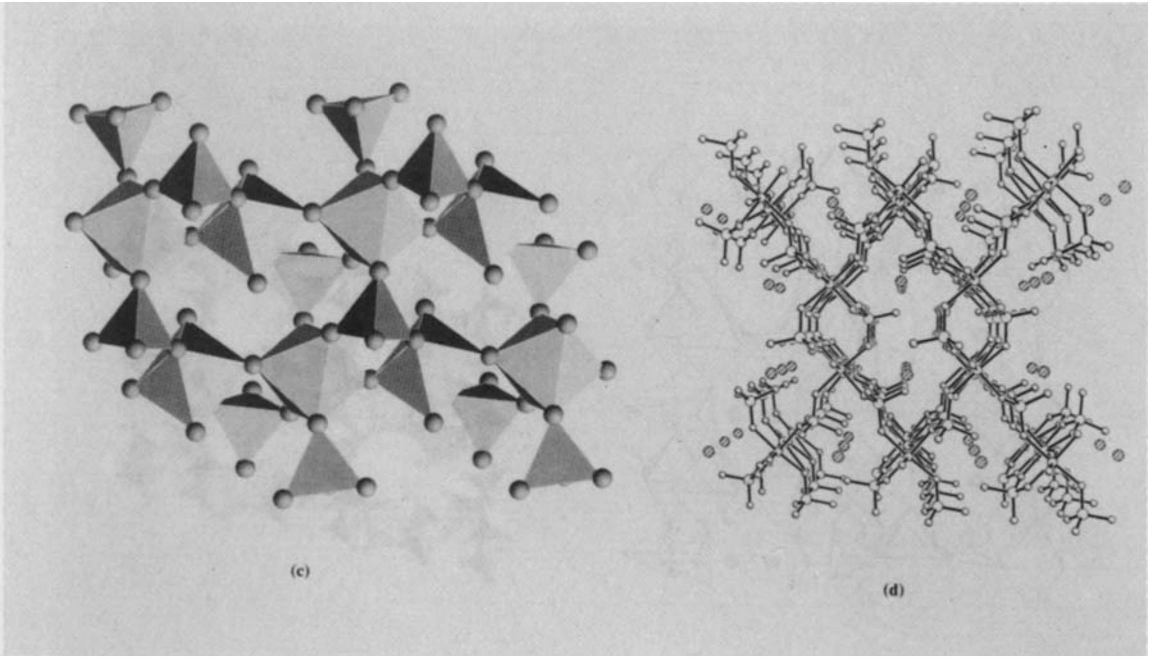
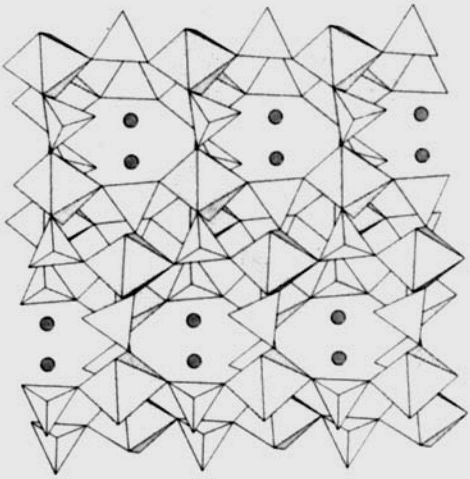
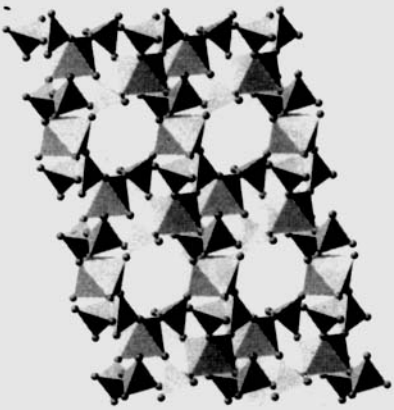


FIGURE 1 Representative structures of V/O/PO_4^{3-} phases incorporating inorganic cations as templates. (a) A polyhedral representation of the structure of $Sr_2[V(PO_4)(HPO_4)_2]$ (**1**) showing the chains of phosphate bridged $\{VO_6\}$ octahedra. (b) A view of the structure of $Rb_{0.5}[VO(PO_4)(H_2O)]$ (**2**) highlighting the one-dimensional $\{V-O-V-O\}_\infty$ chains which provide the framework backbone. (c) A polyhedral representation of the structure of $Cs[(V_2O_3)(HPO_4)_2(H_2O)]$ (**3**) showing the chains of $\{V-O-V-O\}_\infty$ octahedra. (d) A view of the structure of **3** parallel to [001] showing the hydrophilic $\{HPO_4\}$-lined tunnels which accommodate the Cs^+ cations. (e) Polyhedral representation of the structure of $Rb[V(HPO_4)_2]$ (**4**) showing the channels occupied by the Rb^+ cations. (f) Polyhedral representation of the structure of $Cs[V_2(PO_4)(HPO_4)_2(H_2O)_2]$ (**5**) showing the 16-membered V – O – P cycles formed by corner-sharing alternation of four V-octahedra and four P-tetrahedra. (g) A ball and stick representation of the three-dimensional framework of **5** viewed down [001]. (h) The structure of $K_2[(V^{IV}O)_2V^{III}(PO_4)_2(HPO_4)(H_2PO_4)(H_2O)_2]$ (**6**) along the **a** axis highlighting a "step" layer which consists of infinite ribbons six polyhedra in width.

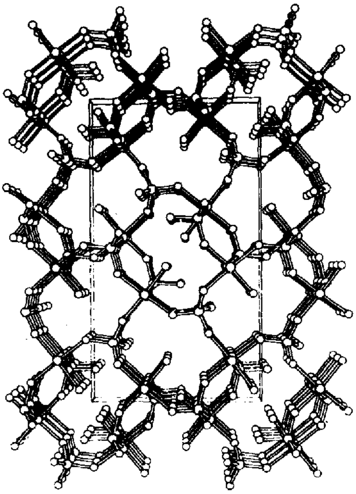

(c)
(d)



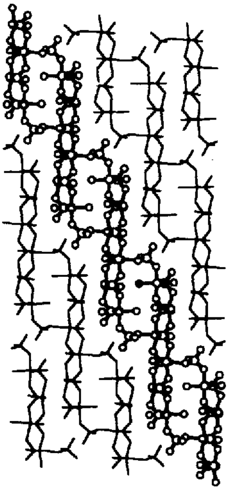
(f)



(e)



(g)



(h)

type vanadium phosphate phases may emerge as more examples become available.

Similarly, modification of the reaction conditions employed in the synthesis of **3** by introduction of vanadium metal as a reductant yields the V(III) composition $Cs[V_2(PO_4)(HPO_4)_2(H_2O)_2]$ (**5**),[56] a material containing an octahedral/tetrahedral network connected in such a way as to produce a structural motif of two fused 8-membered rings in turn fused to two adjacent 16-membered rings. The large V–O–P cycles are generated by corner-sharing alternation of four vanadium octahedra and four phosphorus tetrahedra. The larger 16-membered rings are seen to stack along the axis so as to produce channels, which are occupied by the Cs^+ cations. When viewed along the appropriate axis, the vanadophosphate framework of **5** is seen to consist of layers of one vanadium octahedron plus one phosphorus tetrahedron in thickness, connected through interlamellar phosphorus tetrahedra. The structure may thus be described as a modified lamellar-type.

As illustrated by the structure of **5**, V(III) centers commonly adopt distorted octahedral geometry, a feature of chemistry which may be exploited to disrupt the tendency of V/P/O phases to form the common two-dimensional lamellar frameworks based on corner-sharing of vanadium square pyramids and phosphate tetrahedra. Thus, the introduction of reduced V(III) sites into a predominantly V(IV)/P/O composition should encourage the formation of three-dimensional networks. The structure of $K_2[(VO)_2V(PO_4)_2(HPO_4)(H_2PO_4)(H_2O)_2]$ (**6**) illustrates this role of the V(III) centers.[56] The structure consists of parallel ribbons in which corner-sharing vanadium octahedra and phosphorus tetrahedra alternate. There are three chemically and crystallographically distinct vanadium sites: a six-coordinate oxo-V(IV) site, an octahedral V(III) site, and an unusual square pyramidal oxo-V(IV) site with an additional weak interaction to a phosphate oxygen of a neighboring layer. Comparison of the structure of **6** to that of $K_2[(VO)_2(PO_4)_2(HPO_4)(H_2PO_4)]$[40] reveals the role of the V(III) in the expansion of the step layers from the 4-connect geometry of the latter to the 6-connect motif adopted by **6**.

While inorganic cations as templates provide a useful method for preparing V/P/O phases with open framework structures, the template must be removed in order to gain access to the structural microporosity of these solids. The difficulty arises that the cavities associated with these materials exhibit windows for communication with the environment which are too small to allow easy passage of substrate molecules. In other words, the removal of template results in framework collapse. One strategy for the preparation of open framework solids with accessible microporosity is the introduction of organic templates, which may provide variable and larger cavity dimensions and more readily removed templates.

3. Oxo-Vanadium Phosphates Incorporating Organic Templates

Previous investigations of the Mo/O/PO_4^{3-} system with organic cations as pore-filling entities have established a common structural element—that the relatively less polar molybdenyl groups neighbor the non-polar organic cations while the polar inorganic cations associate with the P–O and P–OH groups of the framework.[5] Thus, these materials are amphiphilic with the crystal packing associated with hydrophilic–hydrophobic interactions. Furthermore, our investigations of the V/O/PO_4^{3-} system cited above indicate that in general V(V)/phosphate and V(IV)/phosphate systems with V/P ratios less than 1:1 incorporate inorganic cations rather readily but not organic cations. We have adopted a number of strategies to induce the incorporation of the organic templates. These rely on the general principle that cation directed synthesis will allow construction of complex three-dimensional networks by exploiting hydrophobic/hydrophilic interactions.

(i) If we assume that the 1:1 V(V, IV)/P systems are too polar to accommodate the organic template, reduction of the V centers to lower oxidation states should provide a framework of reduced polarity. The introduction of V metal as a reactant has dramatically expanded the structural chemistry of this system and has provided a number of unusual V(III)/phosphates and mixed valence V(III,IV)/phosphates of which compound **5** is the most intriguing.

(ii) Variation in V/P ratio provides another approach. By raising the V/P ratio, the vanadyl (V=O) content of the structure may be enhanced. Since M=O moieties are considerably less polar than P–O groups, the tendency of solids rich in M=O units to encapsulate organic templates should be enhanced. This principle has been most successfully exploited in the syntheses of

$K_4(Me_2NH_2)[V_{10}O_{10}(OH)_4(PO_4)_7(H_2O)_2]\cdot 5H_2O$ (**7**), $(H_3NCH_2CH_2NH_3)_{2.5}[V^{III}(VO)_8(OH)_4(HPO_4)_4(PO_4)_4(H_2O)_2]$ (**8**), $(H_3NCH_2CH_2CH_2NH_3)K[(VO)_3(PO_4)_3]$ (**9**) and $(H_3NCH_2CH_2CH_2NH_3)[(VO)_3(OH)_2(PO_4)_2(H_2O)_2]$ (**10**).

Compound **7** represents the first example of a $V/O/PO_4^{3-}$ phase to exhibit direct incorporation of an organic template during synthesis.[58] The structural complexity which may be exhibited by "simple" vanadium phosphate phases is dramatically illustrated by the structure of this species which consists of a unique network of edge- and corner-sharing V(IV) octahedra and square pyramids and phosphate tetrahedra. The structure, shown in Fig. 2(a), contains two recurrent structural motifs of V/P/O solid phases: (V–O–V–O) chains and $\{(VO)_2(\mu_2\text{-}O_2PO_2)_2\}$ units. Unusual structural features on the framework level include the presence of both octahedral and square pyramidal vanadium centers, the incorporation of bridging hydroxy-groups, and the adoption of a monodentate doubly bridging mode $\{(VO)_2(\mu_2\text{-}OPO_3)\}$ through phosphate oxygen donors. Compound **7** provides a striking example of the remarkable potential of self-assembly to produce complex solid state structures with considerable pore volume from simple inorganic components, in this case KVO_3 and H_3PO_4.

The unusual stoichiometry of **7**, together with the hydrophobic/hydrophilic interactions which result from the incorporation of organic and polar cations, result in a "phosphate-deficient" structure with considerable void space. As shown in Fig. 2(a), the structure may be described in terms of a three-dimensional pore framework with non-intersecting tunnels. The K^+ cations and water molecules occupy the smaller hydrophilic channels, while the $Me_2NH_2^+$ groups nestle in the larger, less polar tunnels. As expected, the channels which accommodate the organic cation are associated with the vanadyl $\{V{=}O\}$ groups. A most notable feature of **7** is the spiral nature of the V/P/O framework, resulting in a chiral double helical structural motif for an inorganic material.

While the structure of **7** represents a highly unusual example of organic cation incorporation into a vanadophosphate framework, by judicious choice of reaction conditions a variety of organic templates may be incorporated into such phases. We have noted that the introduction of reduced vanadium into the synthesis of vanadium phosphate materials enhances the flexibility of the connectivity patterns adopted between vandium octahedra and phosphorus tetrahedra, thereby considerably enriching the structural chemistry which may be derived. By disrupting the tendency of V/P/O phases to form two-dimensional lamellar frameworks, the presence of the V(III) sites in the structure encourages the formation of three-dimensional networks with sufficient flexibility of connectivity to incorporate organic cations and thus to exploit hydrophobic/hydrophilic segregation in the lattice. These synthetic principles are illustrated by the structure of $(H_{1.67}en)_3[V^{III}(V^{IV}O)_8(OH)_4(HPO_4)_4(PO_4)_4(H_2O)_2]$ (**8**).[59] The isolation of **8** illustrates, furthermore, the observation that an increase in the V:P ratio appears to favor uptake of organic templates by providing an enhanced concentration of non-polar vanadyl (V=O) moieties.

The V(III)/V(IV) mixed valence material **8** consists of layers constructed from $\{(VO)_2(\mu\text{-}O)(\mu_2\text{-}PO_4)\}$ units connected through $\{V^{III}(H_2O)_2\}$ units. The terminal oxo-groups of the V^{IV} centers of the layers project into the interlamellar region to produce hydrophobic regions, which are occupied by the $(H_3NCH_2CH_2NH3)^{2+}$ cations. In a similar fashion, the pendant –OH groups of the hydrogen phosphate residues project into the interlayer space to provide polar regions occupied by the H_3O^+ cations. As shown in the accompanying figures, the interlamellar volumes are large, a constraint imposed by the need to encapsulate the organic template. While the free diameter of the cavity is as yet unknown, the atom to atom distance defining the cavity is one unit cell length, 18.1 Å. The presence of both inorganic and organic cations induces the interplay of hydrophobic/hydrophilic interactions which result in a connectivity pattern providing for the segregation of polar and non-polar cavities within the lattice.

The importance of such hydrophobic/hydrophilic interactions in the syntehsis of framework solids encapsulating organic guest molecules is dramatized by the isolation of **9**.[60] By exploiting such hydrophobic/hydrophilic partitioning and by introducing low valent vanadium sites into the V/P/O networks to reduce frame-work polarity, a material of significant cavity diameter $(H_3NCH_2CH_2CH_2NH_3)\ K[(VO)_3(PO_4)_3]$ (**9**) was isolated. As shown in Fig. 2(c), the structure is fashioned from vanadium square pyramids and phosphate tetrahedra, to produce binuclear $\{(VO_2(\mu_2\text{-}PO_4)_2\}$ structural motifs which aggregate in such a fashion as to

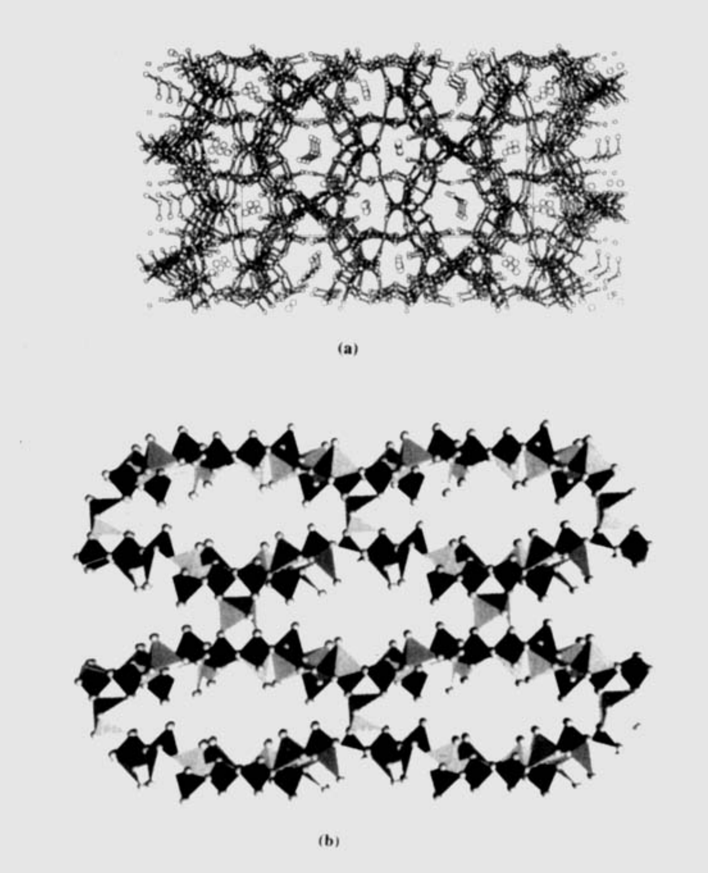
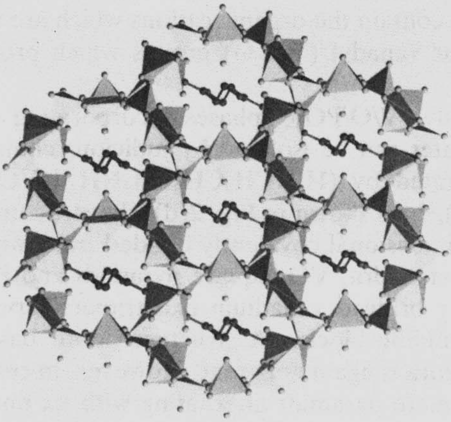
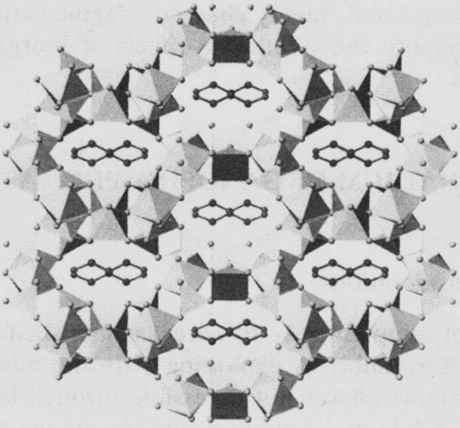


FIGURE 2 Representative structures of V/O/PO$_4^{3-}$ phases incorporating organic cationic templates. (a) A view of the complex three-dimensional framework structure of $K_4(Me_2NH_2)[V_{10}O_{10}(OH)_4(PO_4)_7(H_2O)_2]\cdot 5H_2O$ (**7**) showing the channels occupied by H^+ and $Me_2NH_2^+$ cations. The partitioning of the structure into hydrophilic and hydrophobic domains is apparent. (b) A polyhedral representation of the structure of $(H_2en)_{2.5}[V^{III}(V^{IV}O)_8(OH)_4(PO_4)_4(H_2O)_2]$ (**8**), showing the 18.1 Å cavities occupied by the organic templates. The vestigial layer structure is noteworthy, as is the role of V^{III} octahedra in linking the layers of V^{IV} square pyramids and phosphate tetrahedra. (c) Polyhedral representation of the structure of $(H_3NCH_2CH_2CH_2NH_3)K[(VO)_3(PO_4)_3]$ (**9**), showing the 24-membered rings formed from twelve corner-sharing V and P polyhedra. The fundamental structural motif consists of corner-sharing V-square pyramids in the *anti* configuration. (d) A polyhedral view of the structure of $(H_3NCH_2CH_2CH_2NH_3)[(VO)_3(OH)_2(PO_4)_2(H_2O)_2]$ (**10**) showing the 20-membered rings of two V-square pyramids, four V-octahedra, and four phosphrous tetrahedra which form the periphery of the channels occupied by the organic cation. In contrast to the structure of **9** above, **10** contains hydroxy bridged {VO}-trinuclear units $\{V_3O_3(OH_2)\}$ as the fundamental building block.



(c)



(d)

produce rings of twelve corner-sharing polyhedra. The connectivity of the covalently bonded vanadium phosphate framework generates distinct channels occupied by the $(H_3NCH_2CH_2CH_2NH_3)^{2+}$ cations and K^+ cations. The larger tunnels of approximate diameter 10 Å contain the organic cations which are associated with the less polar vanadyl (V=O) groups which project into these cavities.

Significantly, $V/O/PO_4^{3-}$ phases incorporating exclusively organic templates can be isolated by judicious choice of template, as demonstrated by $(H_3NCH_2CH_2CH_2NH_3)[(VO)_3(OH)_2(PO_4)_2(H_2O)_2]$ (**10**).[61] As shown in Fig. 2(d), the structure of **10** consists of a three-dimensional covalently bonded framework constructed from VO_6 octahedra, VO_5 square pyramids and PO_4 tetrahedra, with hydroxy bridged vanadium oxo trimers serving as the fundamental building blocks. A structural motif based on rings of fused polyhedra is again apparent. However, in contrast to the six vanadium square pyramids alternating with six phosphorus tetrahedra observed for **9**, the rings in **10** are defined by the corner-sharing of two VO_5 square pyramids, four vanadium octahedra and four phosphorous tetrahedra. The structure of **10** demonstrates that by employing small, highly charged organic cations, phases which do not require the stabilizing effects of inorganic cations may be isolated.

THE OXOVANADIUM ORGANOPHOSPHONATE SYSTEM

1. General Considerations

The syntheses of compounds **1–10** were accomplished through the expedient of self-assembly by exploiting hydrothermal techniques to isolate metastable phases not accessible through high temperature synthesis. While this "chimie douce" technique provides numerous synthetic advantages, the rational design of solids by self-assembly from a mixture of precursors is not likely to be totally effective. Furthermore, the interior surfaces of the V/O/phosphate phases discussed above are too polar to accommodate larger organic templates or organic templates with low charge/volume ratios. The use of modified phosphorus framework constituents, such as organophosponates RPO_3^{2-}, can address both of these pitfalls encountered in the synthesis of open framework V/P/O phases. The V/O/organophosphonate system should allow the isolation of simple molecular species which would permit the preparation of larger oligomers and ultimately solid phases by the more coventional synthetic routes of addition or fragment condensation by controlled hydrolysis of the soluble molecular precursors. Likewise, substitution of polar phosphate groups by organophosphonates should provide hydrophobic regions to accommodate the organic constituents. Finally, the properties of $V/O/RPO_3^{2-}$ phases may be modified by presynthesis variation in nature of the substituent R or by postsynthesis derivatization of the R-group.

In this regard, it is noteworthy that the oxovanadium organophosphonate solids, exemplified by $[VO(C_6H_5PO_3)]\cdot H_2O$ whose structure is illustrated in Fig. 3(a), possess structurally well-defined internal void spaces and coordination sites which intercalate alcohols by coordination of the substrate molecule to the vanadium centers of the inorganic V/P/O layer. The shape selectivity of these phases in absorbing alcohols is related to the steric constraints imposed by the organic residues of the phosphonates surrounding the metal sites and to the interplay of hydrophobic and hydrophilic domains in the structure.[31]

2. Molecular Clusters of the $V/O/RPO_3^{2-}$ System

In contrast to the developments in the chemistry of oxovanadium organophosphonate solid phases, the chemistry of molecular systems remains relatively unexplored. However, recent investigations suggest a rich structural chemistry and the possibility of isolating low molecular weight oxovanadium phosphonates which serve as precursors for predictable fragment condensation into higher oligomers.

The simplest molecular species in the V/O/organophosphonate system characterized to date are the binuclear complexes $[(VO)_2Cl_2(H_2O)_2(RPO_3H)_2]$ ($R = -C_6H_5, -CH_3$) and $[(VO)_2Cl_4(t\text{-}C_4H_9PO_3H)_2]^{2-}$.[62] The structure of **11**$\cdot 2[(C_6H_5)_4PCl]$ consists of discrete binuclear units of $[V_2O_2Cl_2(C_6H_5PO_3H)_2(H_2O)_2]$ (**11**), shown in Fig. 4(a), co-crystallizing with $(C_6H_5)_4P^+$ cations and

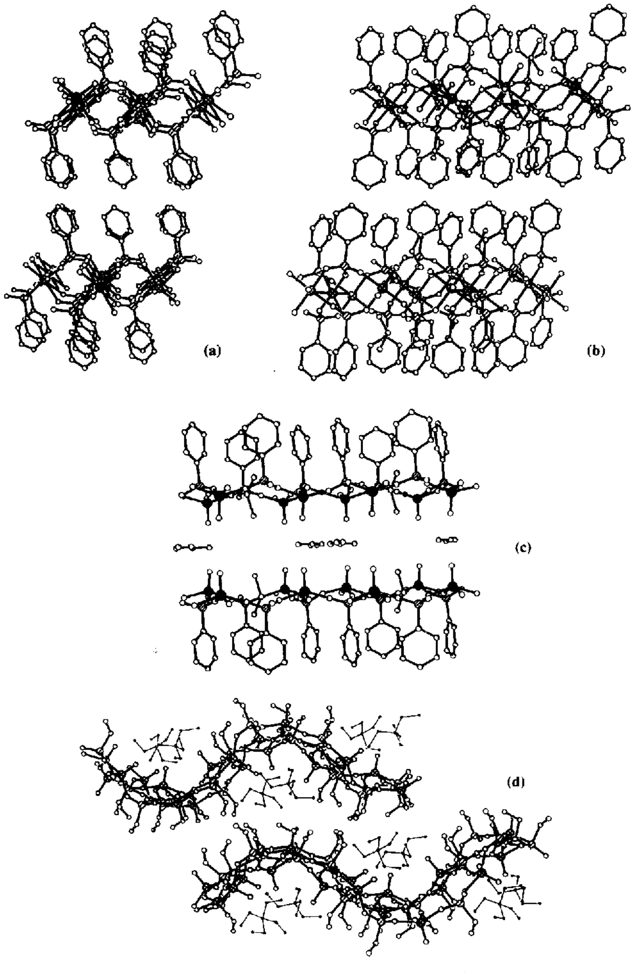
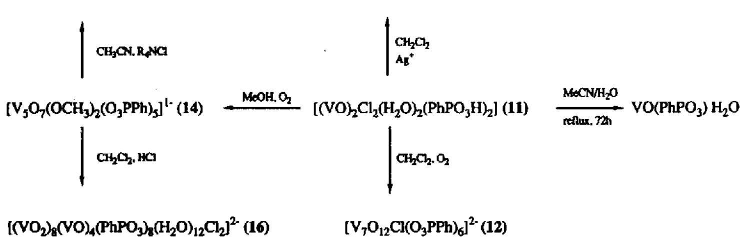


FIGURE 3 Two-dimensional solids of the V/O/organophosphonate system. (a) A view of the structure of $VO(PhPO_3)\cdot H_2O$ showing the alternation of inorganic V/P/O layers and organic bilayers. (b) The structure of $(C_2H_5NH_3)_2[V_3O_3(H_2O)(PhPO_3)_4]$ (**19**), illustrating the gross relationship to the $VO(PhPO_3)\cdot H_2O$ prototype. The locations of the organic templates are noted. In contrast to $VO(PhPO_3)\cdot H_2O$ which exhibits infinite $\{V-O-V-O\}_\infty$ chains in the V/P/O planes, **19** possesses discrete $\{V_3O_3(H_2O)\}$ zig-zag units. (c) The structure of $[Et_2NH_2][Me_2NH_2][V_4O_4(OH)_2(PhPO_3)_4]$ (**20**), showing the unusual registry of layers. Organic cations not only intercalate between inorganic V/P/O layers but also penetrate the V/P/O layers. (d) A view of the structure of $(Et_4N)_2[(VO)_6(OH)_2(H_2O)_2(EtPO_3)_6]$ (**21**), showing the unusual undulating planes produced by the presence of the intercalated organic cations.

Cl^- anions. The overall structure may be described in terms of two vanadium(IV) square pyramids and two phosphonate tetrahedra in a corner-sharing arrangement. The topological relationship of the $[(VO)_2Cl_2(H_2O)_2(RPO_3H)_2]$ species to the infinite $[VO(RPO_3H)(H_2O)]$ sheets of the solid, shown in Fig. 4(b), suggests that the binuclear units of **11** may serve as building blocks for the preparation of solids by condensation/hydrolysis processes involving the ligation of the pendant oxygens of the organophosphonate groups and concomitant loss of HCl and displacement of the aquo ligand.

As anticipated, these binuclear species serve as precursors for condensation into larger oligomers and inorganic solids (Scheme 1). The structures of the unusual molecular anions isolated to date are illustrated in Fig. 4(d)–(i). Several noteworthy features of the chemistry merit discussion. The organization of the clusters about inorganic anionic templates is apparent. While this is a common feature of a majority of the structures, there is sufficient structural versatility to accommodate neutral organic molecules or templates and even metal-bound oxo-groups as in the case of **14**, a structure consisting of a highly unsymmetrical bowl folded about the oxo-group.

A remarkable feature of the chemistry of **14**[63] is the hydrolysis/condensation reaction to form the supercluster $[V_{18}O_{25}(H_2O)_2(PhPO_3)_{20}Cl_4]^{4-}$ (**15**)[64] and the unusual mixed valence cluster $[(V^VO_2)_8(V^{IV}O)_4(H_2O)_{12}(PhPO_3)_8Cl_2]^{2-}$ (**16**). The structural relationship of **15** to $[V_5O_7(PhPO_3)_5]^{1-}$ is apparent, as shown in Fig. 4(e) and (f). Removal of the pendant $\{VO(OCH_3)\}$ group of **14** frees three phosphonate oxygen groups to condense to additional



SCHEME 1

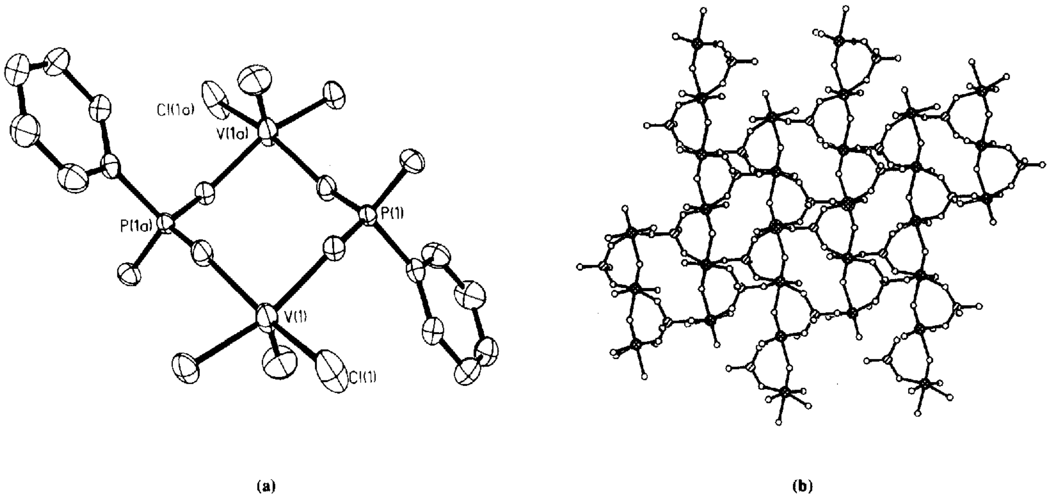
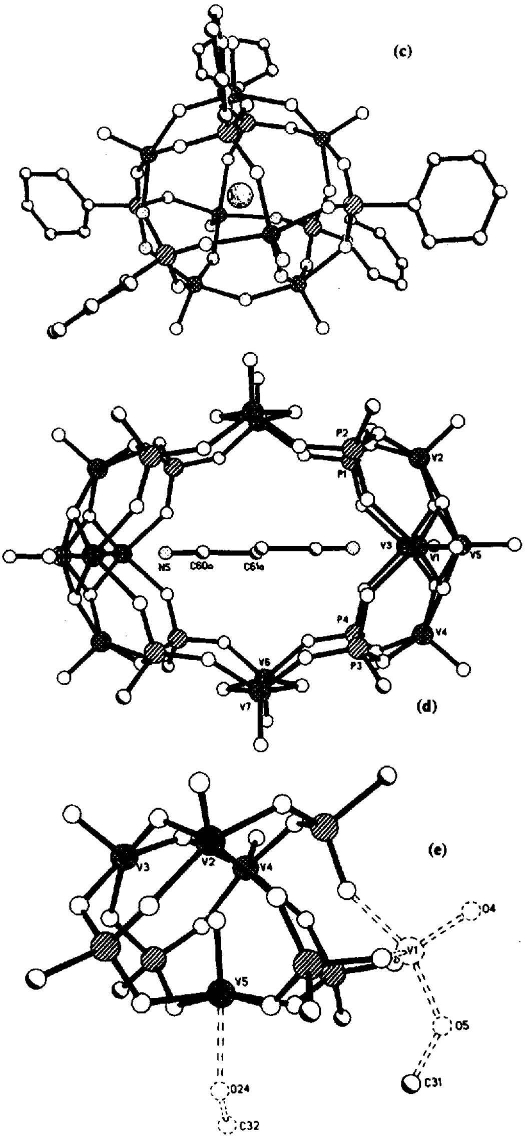
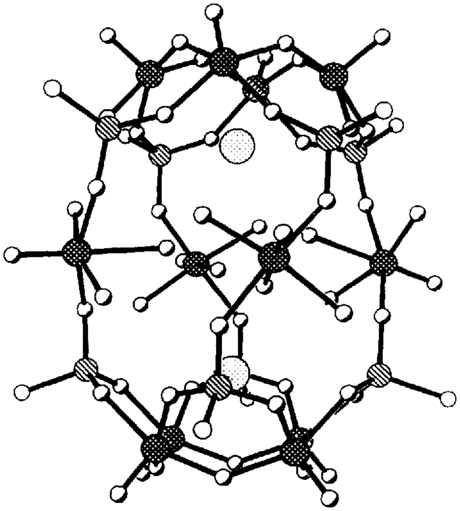
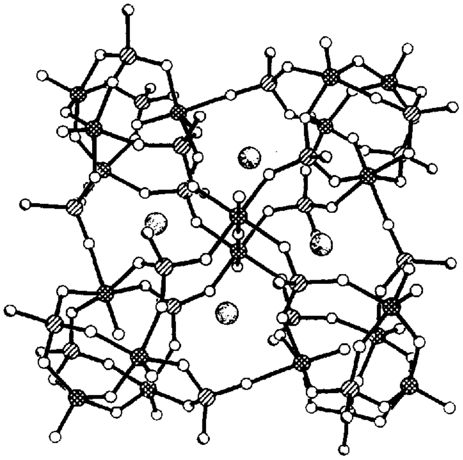


FIGURE 4 Molecular species of the V/O/organophosphonato system. (a) A view of the structure of $[(VO)_2Cl_2(H_2O)_2(PhPO_3H)_2]$ (**11**). (b) A view of the V/O/P plane of $VO(PhPO_3)\cdot H_2O$ (see also Fig. 3a) highlighting the topological relationship to the binuclear unit of **11**. (c) A view of the structure of the $[V_7O_{12}(PhPO_3)_6Cl]^{2-}$ (**12**) molecular anion. (d) A view of the V/O/P shell of $[2CH_3CNV_{14}O_{22}(OH)_4(PhPO_3)_8]^{6-}$ (**13**), showing the locations of the encapsulated CH_3CN molecules. (e) The structure of $[V_5O_7(OCH_3)_2(PhPO_3)_5]^{1-}$ (**14**), highlighting the "pendant" $\{VO(OCH_3)\}^{2+}$ unit and the methoxy group which are displaced in subsequent aggregation processes. (f) The structure of $[V_{18}O_{25}(H_2O)_2(PhPO_3)_{20}Cl_4]^{4-}$ (**15**). The "supercluster" **15** is constricted by the loss of $(OCH_3)^-$ groups and $\{VO(OCH_3)\}^{2+}$ units from four $[V_5O_7(OCH_3)_2(PhPO_3)_5]^{1-}$ and fusion and aggregation about a $\{V_2O(H_2O)_2\}^{8+}$ moiety. (g) A view of the structure of $[(V^VO_2)_8(V^{IV}O)_4(PhPO_3)_8(H_2O)_{12}Cl_2]^{2-}$ (**16**). The structural kinship to the synthetic parent **14** is more remote than that of **15**. (h) A view of the highly symmetrical structure of $[(VO)_6(C_4H_9PO_3)_8Cl]$ (**17**). (i) The structure of $[(VO)_4\{P1P(O)_2OP(O)_2Ph\}_4Cl]^{1-}$ (**18**), illustrating the formation of the diphosphonate ligand $\{RP(O)_2OP(O)_2R\}^{2-}$.

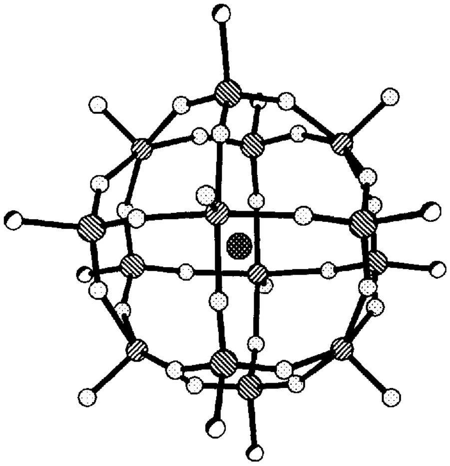

(c)
P2
V2
P1
N5
C60a
C61a
V3
V1
V5
P4
V4
V6
P3
V7
(d)
(e)
V3
V2
V4
O4
V1
O5
V5
C31
O24
C32



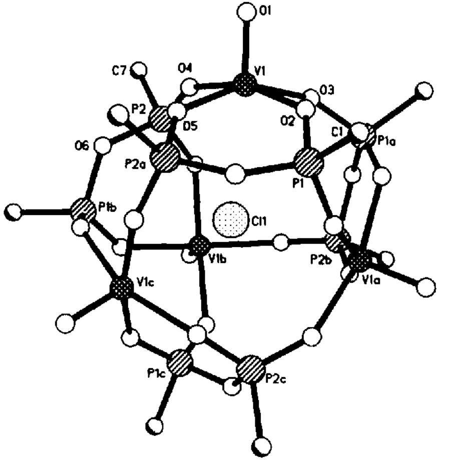
(g)



(f)



(h)


O1
C7
O4
V1
O3
P2
O5
O2
C1
P1a
O6
P2a
P1
Cl1
P1b
V1b
P2b
V1a
V1c
P1c
P2c

(i)

vanadium sites. One phosphonate oxygen group displaces a methoxy group from the site *trans* to the interior-directed V=O unit of a $\{VO(OCH_3)(PhPO_3)_4\}$ center of a second $\{V_4O_6(OCH_3)(PhPO_3)_5\}$ unit while the remaining two P–O groups are utilized in bonding to the central $\{V_2O(H_2O)_2\}^{8+}$ fragment to form the cluster shell. It is noteworthy that the unusual {V=O} units, which are directed toward the interior of the subunit cavities and which were first described for $[V_5O_7(OCH_3)_2(PhPO_3)_5]^{1-}$, are retained in the structure of the supercluster. The $[V_{18}O_{25}(H_2O)_2(PhPO_3)_2Cl_4]^{4-}$ structure may be considered a "cluster of clusters," demonstrating that by exploiting appropriate ligand types, small oligomers may be linked into clusters of nanometer dimensions by more or less rational synthetic routes.

Treatment of **14** with aqueous HCl results in significant reorganization to give **16**, a mixed valence species in which the V(IV) sites are localized in the four bridging $\{VO(H_2O)_4\}$ moieties. In this instance, the incipient V–oxo bounds of the precursor suggested by the interactions of the *endo* V=O group with the V centers of the trinuclear cap appear to direct the formation of the $\{VO_2(PhPO_3)\}_4^{-1}$ capping groups.

We also note that cluster formation is dependent on the organophosphonate substituent, as suggested by the isolation of $[(VO)_6(C_4H_9PO_3)_8Cl]$ (**17**). Finally, the chemical versatility of the system is dramatized by the preparation of $[(VO)_4\{PhP(O)_2OP(O)_2Ph\}_4Cl]$ (**18**), a species in which metal mediated condensation of the organophosphonates has produced the unusual diphosphonate ligand.

3. Solid Phases of the $V/O/RPO_3^{2-}$ System

While the preparation of solid phases of the $V/O/RPO_3^{2-}$ system has required the use of hydrothermal conditions rather than condensation/hydrolysis under conventional conditions, we have succeeded in introducing organic templates into the $V/O/RPO_3^{2-}$ framework to produce a class of novel materials with intercalated organic cations. These are represented by the structures of $(C_2H_5NH_3)_2[V_3O_3(H_2O)(PhPO_3)_4]$ (**19**), $(Et_2NH_2)(Me_2NH_2)[V_4O_4(OH)_2(PhPO_3)_4]$ (**20**) and $(Et_4N)2[(VO)_6(OH)_2(H_2O)_2(EtPO_3)_6]$ (**21**). The structure of **19** is quite similar to that of the prototype $VO(PhPO_3) \cdot H_2O$ and consists of alternating inorganic and organic layers with the organic cationic template occupying tunnels perpendicular to the V/O/P planes. In contrast, in the structure of **20**, the registry of layers has been disrupted such that a layer of $Et_2NH_2{}^+$ cations intercalates between inorganic V/P/O layers, which are in turn sandwiched between bilayers of phenyl groups which project exclusively from one side of metal oxide layer. The second organic cation $Me_2NH_2^+$ penetrates the V/P/O layer requiring an expansion of the $\{V-O-P-O\}_n$ ring motif to the corner-sharing of four vanadium square pyramids and four phosphorus tetrahedra. The most dramatic structural change occurs in the structure of **21** where the registry of ethyl substituents and intercalating Et_4N^+ group produces an undulating plane. While these results are of too recent an origin to draw general conclusions, it is apparent that a diverse structural chemistry of the solid phases will evolve given the sensitivity of structure to substituents, templates and reaction conditions.

CONCLUSIONS

A major challenge facing the synthetic chemist is the preparation of solid materials designed to display a specific set of physical properties. However, the methodology for the preparation on demand of inorganic materials with metastable but persistent extended structures is nearly absent.[65] Nevertheless, the exploitation of molecular concepts and synthetic strategies has resulted in some inroads. The use of solvothermal techniques, condensation/hydrolysis reactions, and template organization of cluster shells or solid frameworks has produced a variety of novel structural types. An unusually rich chemistry is evolving from the $V/O/PO_4^{3-}$ and $V/O/RPO_3^{2-}$ systems, whose solid phases are constructed from the fusing of simple building blocks—vanadium square pyramids and/or octahedra and phosphorus tetrahedra. The major problems are the magnitude of the synthetic parameter space (time, temperature, stoichiometries, nucleation and crystallization rates, templates, substituents, pH, etc.) and the difficulty of attaining actual microporosity. While the broad goal of preparing open solids capable of sorbing substrate molecules which could then undergo selective catalytic reactions at transition metal sites has been partially realized, the removal of template without framework collapse remains a largely unrealized objective. However, the rapidly expanding chemistry of this system suggests that many more examples of such solids will be discovered and that the principles governing their preparations and properties will begin to emerge.

Acknowledgment

This work was supported by NSF Grant Nos. CHE9119910 and CHE9318824 and ACS-PRF 26313-AC3.

References

1. D. E. W. Vaughan, in *Zeolites: Facts, Figures, Future,* eds. P. A. Jacob and R. A. van Santen (Elsevier, Amsterdam, 1989), Vol. 95.
2. J. V. Smith, Chem. Rev. **88**, 149 (1988).
3. (a) R. Szostak, *Molecular Sieves Principles of Synthesis and Identification* (Van Nostrand Reinhold, New York, (1989); (b) W. M. Meier and D. H. Olson, *Atlas of Zeolite Structure* Types (Butterworth, London, 1987).
4. P. J. Fagan and M. D. Ward, Scientific American **48**, 537 (1992); P. J. Fagan, M. D. Ward and J. C. Calabrese, J. Am. Chem. Soc. **111**, 1698 (1989).
5. R. C. Haushalter and L. A. Mundi, Chem. Mater. **4**, 31 (1992).
6. N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements* (Pergamon Press, New York, 1984).
7. L. A. Meyer and R. C. Haushalter, Inorg. Chem. **32**, 1579 (1993).
8. R. C. Haushalter and F. W. Fai, J. Solid State Chem. **76**, 218 (1988).
9. R. C. Haushalter, J. Chem. Soc., Chem. Commun. 374 (1987).
10. R. C. Haushalter and F. W. Lai, Angew. Chem. **101**, 802 (1989).
11. E. W. Corcoran, Inorg. Chem. **29**, 157 (1990).
12. L. A. Mundi and R. C. Haushalter, Inorg. Chem. **29**, 2881 (1990); R. C. Haushalter, K. G. Strohmaier and F. W. Lai, Science **246**, 1289 (1989); L. A. Munci, K. G. Strohmaier, D. P. Goshorn and R. C. Haushalter, J. Am. Chem. Soc. **112**, 8182 (1990); H. E. King, Jr., L. A. Mundi, K. G. Strohmaier and R. C. Haushalter, J. Solid State Chem. **92**, 1 (1991); R. C. Haushalter, L. A. Mundi and K. G. Strohmaier, Inorg. Chem. **30**, 153 (1991); R. C. Haushalter, L. A. Mundi, K. G. Strohmaier and H. E. King, Jr., J. Solid State Chem. **92**, 154 (1991).
13. Numerous zeolitic and layered materials containing phosphate tetrahedra as a building block have been reported. See for example: S. L. Suib, Chem. Rev. **93**, 803 (1993), and references therein.
14. Metal organophosphonate chemistry is extremely rich[15,16] and is represented by monomolecular coordination complexes,[17] molecular clusters,[18–20] one dimensional solid,[21] and layered materials.[22,24] Extensive investigations have been

reported on layered phosphonates of divalent,[25–28] trivalent[29] and tetravalent elements.

15. Y. Zhang and A. Clearfield, Inorg. Chem. **31**, 2821 (1992), and references therein.
16. D. Rong, H.-G. Hong, Y. I. Kim, J. S. Kreuger, J. E. Mayer and T. E. Mallouk, Coord. Chem. Rev. **97**, 237 (1990).
17. E. T. Clark, P. R. Rudolf, A. E. Martell and A. Clearfield, Inorg. Chim. Acta **164**, 59 (1989).
18. G. Cao, R. C. Haushalter and K. G. Strohmaier, Inorg. Chem. **32**, 127 (1993), and references therein.
19. (a) G. Huan, V. W. Day, A. J. Jacobson and D. P. Goshorn, J. Am. Chem. Soc. **113**, 3188 (1991); (b) G. Huan, A. J. Jacobson and V. W. Day, Angew. Chem. Int. Ed. Engl. **30**, 422 (1991).
20. A. Müller, K. Hovemeier and R. Rohlfing, Angew. Chem. Int. Ed. Engl. **31**, 1192 (1992).
21. B. Bujoli, P. Palvadeau and J. Rouxel, Chem. Mater. **2**, 582 (1990).
22. G. Cao, R. C. Haushalter and K. G. Strohmaier, Inorg. Chem. **32**, 127 (1993), and references therein.
23. A. Clearfield, Comments Inorg. Chem. **10**, 89 (1990).
24. G. Cao, H. Lee, V. M. Lynch and T. E Mallouk, Inorg. Chem. **27**, 2781 (1988).
25. C. Bhardwaj, H. Hu and A. Clearfield, Inorg. Chem. **32**, 4294 (1993).
26. J. LeBideau, B. Bujoli, A. Jouanneaux, C. Payen, P. Palvadeau and J. Rouxel, Inorg. Chem. **32**, 4617 (1993).
27. K. Martin, P. J. Squattorito and A. Clearfield, Inorg. Chim. Acta **155**, 7 (1989).
28. G. Cao and T. E. Mallouk, Inorg. Chem. **30**, 1434 (1991).
29. G. Cao, V. M. Lynch, J. S. Swinnea and T. E. Mallouk, Inorg. Chem. **29**, 2112 (1990).
30. G. Alberti, M. Casciola and R. K. Biswas, Inorg. Chim Acta **201**, 207 (1992), and references therein.
31. G. Huan, A. J. Jacobson, J. W. Johnson and E. W. Corcoran, Jr., Chem. Mater. **2**, 91 (1990).
32. G. Huan, J. W. Johnson and A. J. Jacobson, Chem. Mater. **2**, 719 (1990).
33. G. Alberti, M. Casciola, R. Vivani and R. K. Biswas, Inorg. Chem. **32**, 4600 (1993).
34. G. Centi, F. Trifiro, J. R. Ebner and V. M. Franchetti, Chem. Rev. **88**, 55 (1988).
35. B. L. Hodnett, Catal. Rev. Sci. Eng. **27**, 373 (1985).
36. H. R. Tietze, Aust. J. Chem. **34**, 2035 (1981).
37. (a) A. Patter, A. R. Saple and R. Y. Kelken, J. Chem. Soc., Chem. Commun. 356 (1991), and references therein; (b) C. Montes, M. E. Davis, B. Murray and M. Narayana, J. Phys. Chem. **94**, 6425 (1990); (c) L. Benes, J. Votinsky, J. Kalousova and J. Kilkorka, Inorg. Chim. Acta **114**, 47 (1986); (d) K. Beneke and G. Lagaly, Inorg. Chem. **22**, 1503 (1983); (e) J. W. Johnson, A. J. Jacobson, J. F. Brody and S. M. Rich, Inorg. Chem. **21**, 3820 (1982); (f) M. Martinez-Lara, L. Moreno-Real, A. Jimenez-Lopez, S. Bruque-Gomez and A. Rodriquez-Garcia, Mater. Res. Bull. **21**, 13 (1986); (g) J. W. Johnson and A. J. Jacobson, Angew. Chem. **95**, 422 (1983); (h) M. R. Antonio, R. L. Barbour and P. R. Blum, Inorg. Chem. **26**, 1235 (1987); (i) M. Martinez-Lara, A. Jimenez-Lopez, L. Moreno-Real, S. Bruque, B. Casal and E. Ruiz-Hitzky, Mater. Res. Bull **20**, 549 (1985); (j) G.-E. Matsubazaski, S. Ohta and S. Okimo, Inorg. Chim. Acta **184**, 47 (1991).

38. J. W. Johnson, A. J. Jacobson, W. M. Butler, S. E. Rosenthal, J. F. Brody and J. T. Lewandowski, J. Am. Chem. Soc. **111**, 381 (1989).
39. $Zn_2VO(PO_4)_2$: K. H. Lii and H. J. Tsai, J. Solid State Chem. **90**, 291 (1991); $Cs_2V_3P_4O_{17}$: K. H. Lii, Y. P. Wang and S. L. Wang, J. Solid State Chem. **80**, 127 (1989); β-$K_2V_3P_4O_{17}$: K. H. Lii, H. J. Tsai and S. L. Wang, J. Solid State Chem. **87**, 396 (1990); $A_2VOP_2O_7$ (A = Cs, Rb): K. H. Lii and S. L. Wang, J. Solid State Chem. **82**, 239 (1989); AVP_2O_7 (A = Li-Cs): K. H. Lii, Y. P. Wang, Y. B. Chen and S. L. Wang, J. Solid State Chem. **86**, 143 (1990), and references therein; $NaVOPO_4$: K. H. Lii, C. H. Li, T. M. Chen and S. L. Wang, Z. Kristallogr. **197**, 67 (1991); $RbV_3P_3O_{17+x}$: K. H. Lii and C. S. Lee, Inorg. Chem. **29**, 3298 (1990).
40. $A_{0.5}VOPO_4 \cdot xH_2O$ (A = Na, x = 2.0; A = K, x = 1.5): S. L. Wang, H. Y. Kang, C. Y. Cheng and K. H. Lii, Inorg. Chem. **30**, 3496 (1991); $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$: K. H. Lii and H. J. Tsai, Inorg. Chem. **30**, 446 (1991); $K_2(VO)_3(HPO_4)_4$: K. H. Lii and H. J. Tsai, J. Solid State Chem. **91**, 331 (1991).
41. $LiVOPO_4$: A. V. Lavrov, V. P. Nikolaev, G. G. Sadikov and M. A. Porai-Koshits, Sov. Phys. Dokl. (Engl. Transl.) **27**, 680 (1982).
42. $NH_4(VO)(HPO_4)$: K. H. Lii, N. S. Wu, and B. R. Chen, J. Solid State Chem. **97**, 283 (1992).
43. $Ca_2V(PO_4)(HPO_4)_2 \cdot H_2O$ and $Ca_2V(PO_4)(P_2O_7)$: K. H. Lii, N. S. Wen, C. C. Su and B. R. Chen, Inorg. Chem. **31**, 439 (1992); $Cs_3V_3P_{12}O_{36}$: A. V. Lavrov and V. P. Nikolaev.
44. A. Stein, S. W. Keller and T. E. Mallouk, Science **259**, 1558 (1993).
45. M. Figlarz, Chim. Scripta **28**, 3 (1988), and references therein.
46. J. Rouxel, Chim. Scripta **28**, 33 (1988); J. Livage, Chim. Scripta **28**, 9 (1988).
47. R. A. Laudise, Chem. Eng. News, Sept. 28, 30 (1987).
48. H. Dislich, Angew. Chem. Int. Ed. Eng. **10**, 363 (1971).
49. P. C. Bradley, Chem. Rev. **89**, 1317 (1989).
50. L. L. Hench and J. K. West, Chem. Rev. **90**, 33 (1990).
51. (a) M. T. Pope and A. Müller, Angew Chem. Int. Ed. Engl. **30**, 34 (1991), and references therein; (b) M. T. Pope, *Heteropoly and Isopoly Oxometalates* (Springer-Verlag, New York, 1983).
52. H. C. Haushalter and J. Zubieta, unpublished results.
53. K.-H. Lii, T.-C. Lee, S.-N. Liu and S.-L. Wang, J. Chem. Soc., Dalton Trans. 1051 (1993); the solid is improperly formulated as a V(IV) rather than a V(III) species.
54. Z. Wang, H. C. Haushalter, Q. Chen and J. Zubieta, unpublished results.
55. I. Tordjman, R. Masse and J. C. Guitel, Z. Krist. **139**, 103 (1976).
56. R. C. Haushalter, Z. Wang, M. E. Thompson and J. Zubieta, Inorg. Chem. **32**, 3700 (1993).
57. R. C. Haushalter, Z. Wang, M. E. Thompson, J. Zubieta and C. J. O'Connor, Inorg. Chem. **32**, 3966 (1993).
58. V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta and C. J. O'Connor, Science **259**, 1596 (1993).
59. V. Soghomonian, Q. Chen, R. C. Haushalter and J. Zubieta, Angew. Chem. Int. Ed. Engl. **32**, 610 (1993).
60. V. Soghomonian, Q. Chen, R. C. Haushalter and J. Zubieta, Chem. Mater. **5**, 1595 (1993).
61. V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta and C. J. O'Connor, Chem. Mater. **5**, 1690 (1993).

62. Q. Chen, J. Salta and J. Zubieta, Inorg. Chem. **32**, 4485 (1993).
63. Q. Chen and J. Zubieta, Angew. Chem. Int. Ed. Engl. **32**, 261 (1993).
64. J. Salta, Q. Chen, Y.-D. Chang and J. Zubieta, Angew. Chem. Int. Ed. Engl. **33** (1994).
65. R. Hoffmann, Scientific American, 66 (1993).