

## Template Symmetry Effect in Open-framework Synthesis: a New Vanadium(IV) Phosphate

Xianhui Bu, Pingyun Feng and Galen D. Stucky\*

Chemistry Department, University of California at Santa Barbara, Santa Barbara, CA 93106, USA

The template symmetry effect in open-framework syntheses is demonstrated in a newly synthesized vanadium(IV) phosphate encapsulating organic piperazine dications; the hydrothermal synthesis and X-ray crystal structure are described; the structure adopted suggests that inorganic condensation around the organic molecules is dictated by the template molecular symmetry.

Framework materials based on transition metal phosphates and arsenates have received increasing attention.<sup>1-4</sup> The variable coordination numbers and oxidation states of transition-metal sites are potentially useful for a number of chemical processes such as absorption and redox reactions. The vanadium phosphate system is one example of the compositional and structural diversity of transition metal framework structures.

In our studies of the effect of the organic template molecular symmetry on the condensation of the inorganic host phase,<sup>5</sup> a new open-framework vanadium phosphate encapsulating piperazine (pipz) dications has been synthesized. The symmetry of the framework shows that the inorganic condensation around the organic molecules is determined by the symmetry of organic guest molecules.

Crystals of VPO–pipz were grown from a mixture of NaVO<sub>3</sub>, V, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>O and piperazine in a molar ratio of 1.0:0.5:5.17:476:0.71. A dark-blue gel was formed after stirring the mixture for about 15 min. The mixture was then heated at 170 °C for 7 days in a Teflon-coated steel autoclave. The product was recovered by filtration and washed with deionized water. Light-blue needle-like crystals were obtained.

The crystal structure was solved by heavy-atom methods with data collected on a Huber four-circle diffractometer.† Second harmonic generation measurements using powdered samples showed a very weak signal which confirms the choice of the non-centrosymmetric space group *Cm*.

The asymmetric unit is [VO(H<sub>2</sub>O)<sub>3</sub>]<sub>0.5</sub>[VO(H<sub>2</sub>O)]<sub>0.5</sub>(VO)(PO<sub>4</sub>)(HPO<sub>4</sub>)(C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>H<sub>4</sub>)<sub>0.5</sub> (Fig. 1). There are four crystallographically unique vanadium cations. Each vanadium has a

short V=O bond with a bond distance ranging from 1.578 to 1.639 Å. For atoms V(1) and V(2), there is a water molecule *trans* to the V=O bond while V(3) and V(4) share their vanadyl oxygen atoms to form infinite *trans* (V–O)<sub>n</sub> chains. All vanadium cations, vanadyl oxygen atoms and water molecules *trans* to them are located on the crystallographic mirror plane. Also located on the mirror plane are the NH<sub>2</sub> groups of the template piperazine molecules.

Four unique vanadium octahedra share their corners to different extents. Only two corners of V(1) octahedra and four corners of V(2) octahedra are shared with adjacent phosphate tetrahedra while all six corners of V(3) and V(4) octahedra are shared, four of which with phosphate groups. Despite such a difference, all the octahedra have a similar VO<sub>6</sub> geometry typical for V<sup>4+</sup> cations. The V<sup>4+</sup> oxidation state for all four unique vanadium cations is supported by valence sum calculations.<sup>6</sup>

The three-dimensional framework structure is built from columns of vanadium octahedra held together by bridging phosphate groups. Along the *c* direction, there are columns of piperazine rings and three different vanadium columns containing either all V(1) octahedra, all V(2) octahedra, or V(3)/V(4) vanadyl chains. These four different columns are located on the same mirror planes (*y* = 0 or *y* = 1/2) and alternate along the *a* direction. There is an offset of two columns when the row of alternating columns is translated half the cell distance along the *b* direction (Fig. 2).

Piperazine dications are ordered at the intersections of two interconnected channels with elliptical eight-ring openings (for channels along the *c* direction) and ten-ring openings (for channels along the *b* direction). The eight-ring openings are partially obstructed with two dangling hydroxy groups (Fig. 2) while the ten-ring openings are slightly blocked by one vanadyl oxygen atom and one water molecule on V(2) octahedra.

Since the mirror symmetry element of the inorganic lattice coincides with that of the organic molecules, the symmetry of the piperazine molecules templates the formation of the framework structure around them, *i.e.* the framework self-

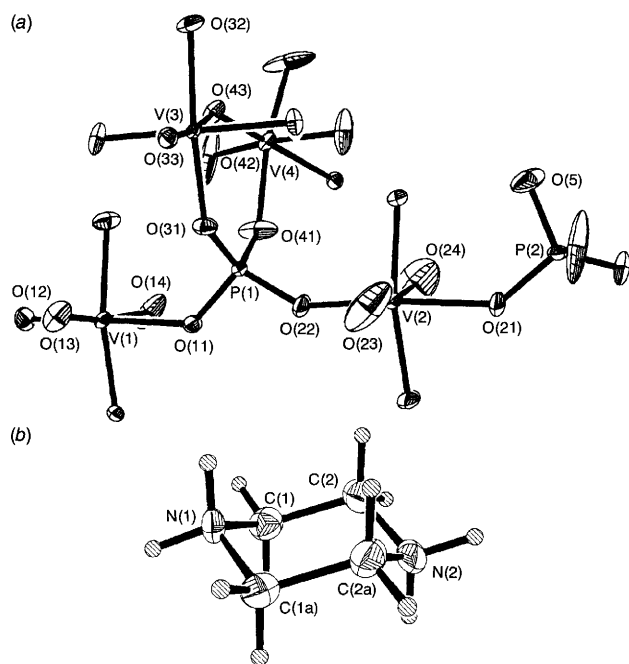


Fig. 1 ORTEP view of vanadium and phosphorus polyhedra (a) and piperazine dications (b)

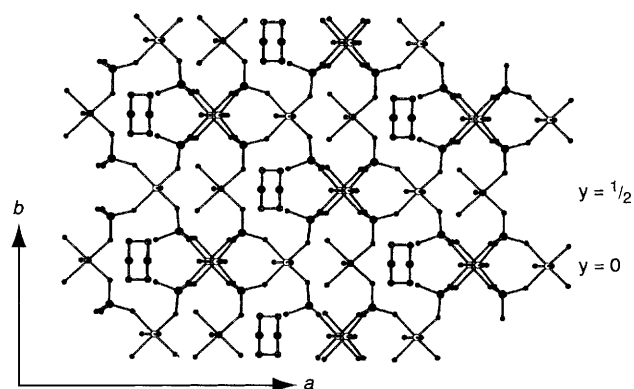
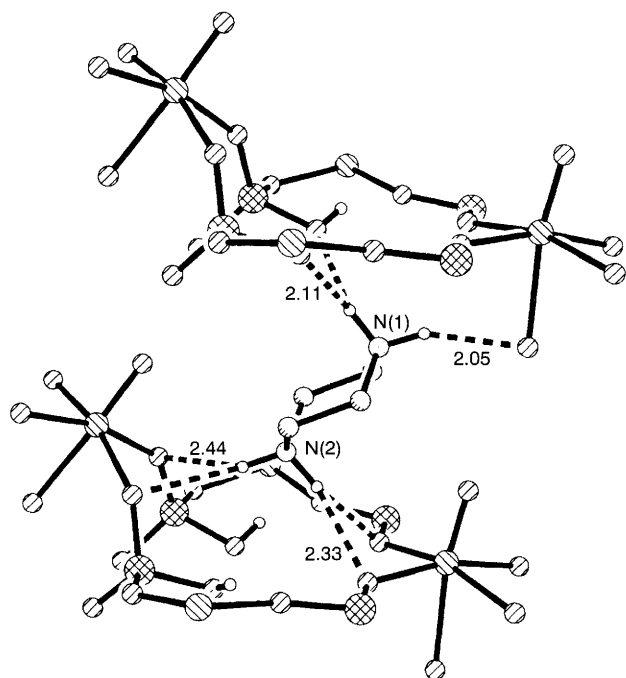


Fig. 2 Projection down the *c* axis showing mirror planes (*y* = 0, 1/2) passing through all vanadium octahedra and template rings. Columns of vanadium octahedra and template rings alternate along the *a* axis.

assembles to conform to the mirror symmetry of the piperazine molecules.

The guest–host interaction involved in the above structure-directing effect appears to consist of one two-centre hydrogen bond and one three-centre hydrogen bond (Fig. 3). The two-centre hydrogen bond (N–H...O) is between one N–H group on N(1) and H<sub>2</sub>O *trans* to V=O on V(1) [N(1)...O 2.939 Å]. The three-centre hydrogen bonding involves one N–H group on N(1) and two hydroxy groups on P(2) tetrahedra [N(1)...O 2.896 Å]. The framework oxygen distribution around N(2) suggests that two N–H bonds on N(2) atoms could only adopt three-centre hydrogen bonding. However, the shortest distance from N(2) to the adjacent oxygens is 3.117 Å, which appears too long for effective hydrogen bonding. Based on hydrogen positions calculated with a N–H distance of 0.95 Å, estimated H...O distances are shown in Fig. 3.

The symmetry matching between the host lattice and the organic template is an important feature of the present compound. We have also synthesized two new zincophosphates templated with piperazine mono- and di-cations respectively (ZnPO–pipz<sup>+</sup> and ZnPO–pipz<sup>2+</sup>). Both structures (space group:



**Fig. 3** Short contacts and hydrogen bonding between guest N–H groups and framework oxygen atoms viewed down [010]. Two inorganic clusters are related by the unit-cell *c* translation and display the mirror symmetry which passes through both clusters and piperazine molecules.

*C2/c*) have the well-known sodalite-type framework topology. In ZnPO–pipz<sup>+</sup>,<sup>5</sup> the piperazine monocations are located at the centre of the interrupted sodalite cage which has inversion centre symmetry. In ZnPO–pipz<sup>2+</sup>,<sup>5</sup> the piperazine dications are located inside the expanded sodalite cage with a two-fold axis. Since the chair conformation of piperazine has point group symmetry *2/m*, which consists of three symmetry elements (*i*, *2*, *m*), we have so far demonstrated that each individual symmetry element of the piperazine molecule can exhibit structure directing effects on the self-assembly of inorganic phases. All three crystals have monoclinic symmetry as determined by the piperazine molecules.

To be considered as symmetry matching, the symmetry element of the organic guest molecule must be one of the crystallographic symmetries of the inorganic framework. However, it is not necessary for the inorganic lattice to adopt the full symmetry of the templating molecules. An individual symmetry element can clearly exhibit structure directing effects as shown above. Which symmetry element is active in the structure directing effect is affected by other factors such as charge matching as demonstrated in the syntheses of ZnPO–pipz<sup>+</sup> and ZnPO–pipz<sup>2+</sup>. The mode of condensation of the inorganic framework is a multiparameter phenomenon which still requires further study.

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#### Footnote

† Crystal data for [VO(H<sub>2</sub>O)<sub>3</sub>][VO(H<sub>2</sub>O)](VO)<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(HPO<sub>4</sub>)<sub>2</sub> (C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>H<sub>4</sub>), *M* = 809.88, space group *Cm*, *a* = 17.399(6), *b* = 9.479(3), *c* = 7.055(2), β = 108.026(2)°, *V* = 1106.5(6) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 2.43 g cm<sup>-3</sup>, transparent blue needle, crystal size 0.58 × 0.067 × 0.033 mm<sup>3</sup>, λ (Mo-Kα), 0.71073 Å, μ = 1.985 mm<sup>-1</sup>, empirical absorption correction, *T*<sub>min</sub> = 0.69, *T*<sub>max</sub> = 0.75, θ<sub>max</sub> = 60°, *R* = 0.029, *wR* = 0.036, GOF = 1.64 for 189 parameters and 1613 unique reflections with *I* > 2.5 σ(*I*).

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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