

# Synthesis and Structure Determination of the Disordered V<sup>V</sup>-P Compound (NH<sub>4</sub>)<sub>2</sub>V<sup>IV</sup>O(V<sub>2-x</sub>P<sub>x</sub>O<sub>7</sub>)

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Orange crystals of (NH<sub>4</sub>)<sub>2</sub>V<sup>IV</sup>O(V<sub>2-x</sub>P<sub>x</sub>O<sub>7</sub>) were synthesized hydrothermally. Their structure was solved by X-ray diffraction in the noncentrosymmetric tetragonal space group *P4* (No. 75)  $a = 8.629(2)$  Å,  $c = 5.648(4)$  Å,  $Z = 2$ ,  $R1(F_0) = 0.0495$ ,  $\omega R2(F_0^2) = 0.1125$  for 1747 independent reflections. The chemical analysis indicates the presence of phosphorus in the material with a V/P ratio close to 2. The X-ray structural determination confirms the fresnoite-type structure with a disordered occupation of the tetrahedral site by the V<sup>V</sup> and P atoms. © 1996 Academic Press, Inc.

## INTRODUCTION

The hydrothermal synthesis of vanadium phosphate was initiated by the pioneer work of Jacobson *et al.* (1–3). Using this technique, we have recently described two new types of vanadium mixed valence oxides formulated (V<sup>IV</sup>O)(V<sup>V</sup>O<sub>4</sub>), 0.5 diamine (4, 5) using piperazine, ethylenediamine, or 1,3-diaminopropane as organic intercalates. In these two-dimensional structures, the ratio V<sup>IV</sup>/V<sup>V</sup> is one and the V<sup>IV</sup> atoms are fivefold coordinated whereas V<sup>V</sup> exhibits a tetrahedral coordination. The complete substitution of V<sup>V</sup> atoms by phosphorus at the tetrahedral sites does not retain the original structural type leading to the two-dimensional structure of (V<sup>IV</sup>O)(PO<sub>4</sub>), 0.5 piperazine (6).

Such an example of total substitution is already encountered with the compounds of the fresnoite type A<sub>2</sub>(V<sup>IV</sup>O)(V<sub>2</sub>O<sub>7</sub>)(A = K, Rb, Cs, NH<sub>4</sub>) (7–9). It leads either to the isotopic compound (NH<sub>4</sub>)<sub>2</sub>V<sup>IV</sup>O(P<sub>2</sub>O<sub>7</sub>) (10) or to two new phases when A is sodium (11) or heavy alkaline ions (12).

This paper deals with the synthesis and the structure determination of (NH<sub>4</sub>)<sub>2</sub>VO(V<sub>2-x</sub>P<sub>x</sub>O<sub>7</sub>), the first compound of the fresnoite type showing a partial and disordered occupation of the tetrahedral site by the V<sup>V</sup> and P atoms.

## EXPERIMENTAL

### Synthesis

The title compound was prepared by hydrothermal synthesis under autogeneous pressure. The reactants were NH<sub>4</sub>VO<sub>3</sub> (Carlo Erba, 99.5%), distilled water, H<sub>3</sub>PO<sub>4</sub> (Pro-labo RP Normapur, 85%), and hexamethylenetetramine (Merck, 99%) introduced in this order with a molar ratio 1:80:1:1. The corresponding mixture was placed in a Teflon lined stainless steel autoclave, unstirred at 453 K for 24 h. The pH of the medium increased from 2–3 to 7–8 during the reaction. The resulting product was washed with water and then dried in air at room temperature. (NH<sub>4</sub>)<sub>2</sub>VO(V<sub>2-x</sub>P<sub>x</sub>O<sub>7</sub>) was obtained pure with a yield of about 50%; as well formed orange crystals whose external habitus (performed on a HITACHI S2300) is shown in Fig. 1.

The thermogravimetric analysis (conducted under Ar flow with a SETARAM TGDTA92 apparatus) showed decomposition at 350°C with a variation in weight of 17.4% corresponding to the loss of one water and two ammoniac molecules (% th. = 17.5). At 500°C, the resulting product was amorphous.

The chemical analysis was first determined by microanalysis on a JEOL 2010 TEM equipped with a KEVEX energy dispersive X-ray spectrometer. Analysis of numerous crystals lead to a V/P ratio close to 2, not in agreement with the known fresnoite compounds A<sub>2</sub>V<sub>3</sub>O<sub>8</sub> or A<sub>2</sub>VO(P<sub>2</sub>O<sub>7</sub>). This result was confirmed by a density measurement performed with a 1305 Micromeritics multipycnometer under He flow. For the pure vanadium oxide (NH<sub>4</sub>)<sub>2</sub>VO(V<sub>2</sub>O<sub>7</sub>), the result should be 2.504 g · cm<sup>-3</sup>; for the diphosphate (NH<sub>4</sub>)<sub>2</sub>VO(P<sub>2</sub>O<sub>7</sub>), it should be 2.188 g · cm<sup>-3</sup>. The measured density 2.35(2) g · cm<sup>-3</sup>, as well as the EDX results, lead us to propose the chemical formula (NH<sub>4</sub>)<sub>2</sub>VO(V<sub>2-x</sub>PO<sub>7</sub>) where  $x \approx 1$ .

### Structure Determination

A suitable crystal was selected for the data collection on a Siemens AED2 four-circle diffractometer using MoK $\alpha$

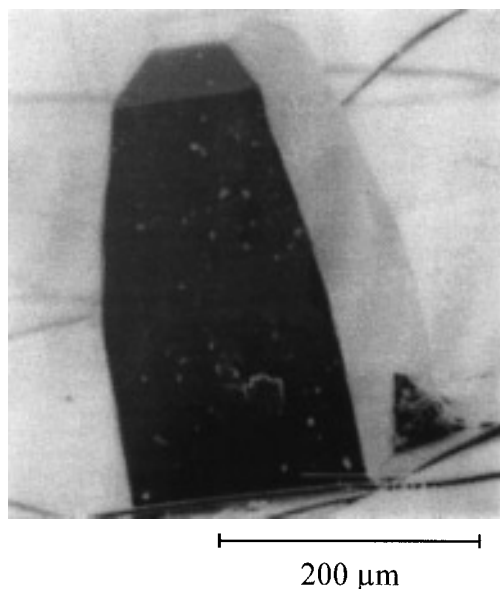


FIG. 1. Scanning electron micrograph of  $(\text{NH}_4)_2\text{VO}(\text{V}_{2-x}\text{P}_x\text{O}_7)$ .

radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Its quality was first checked by Laue photographs. The conditions for data collection are summarized in Table 1.

The title compound is tetragonal with lattice parameters similar to those expected in the fresnoite type. However,

TABLE 1  
Crystal Data and Structure Refinement  
for  $(\text{NH}_4)_2\text{VO}(\text{V}_{2-x}\text{P}_x\text{O}_7)$

|   |  |
|---|--|
| Chemical formula                        | $(\text{NH}_4)_2\text{VO}(\text{V}_{2-x}\text{P}_x\text{O}_7)$ |
| Formula weight                          | 297  |
| Temperature                             | 293 K  |
| Wavelength (MoK $\alpha$ )              | 0.71073 $\text{\AA}$   |
| Crystal system                          | Tetragonal   |
| Space group                             | $P4$ (No. 75)  |
| Unit cell determination                 | 30 reflections ( $30 \leq 2\theta \leq 40^\circ$ )             |
| Unit cell dimensions                    | $a = 8.629(2) \text{ \AA}$ , $c = 5.648(4) \text{ \AA}$        |
| Volume/Z                                | $420.5(3) \text{ \AA}^3/2$                                     |
| Density (calculated)                    | $2.346 \text{ g/cm}^3$   |
| Density (measured)                      | $2.35(2) \text{ g/cm}^3$                                       |
| Absorption coefficient                  | $2.241 \text{ mm}^{-1}$  |
| $F(000)$                                | 294  |
| Crystal size                            | $0.17 \times 0.18 \times 0.34 \text{ mm}$                      |
| $\theta$ range for data collection      | $2.35^\circ$ to $35.0^\circ$                                   |
| Index ranges                            | $-9 \leq h \leq 9$ , $0 \leq k \leq 13$ , $-9 \leq l \leq 9$   |
| Standard measurements                   | 2 4 0; -4 2 0; 0 0 3   |
| Maximum intensity variation             | $\leq 1.1\%$   |
| Reflections collected                   | 2000   |
| Independent reflections                 | 1747 [ $R(\text{int}) = 0.007$ ]                               |
| Refinement method                       | Full-matrix least-squares on $F^2$                             |
| Data/restraints/parameters              | 1747/10/77   |
| Goodness-of-fit on $F^2$                | 1.399  |
| Final $R$ indices [ $I > 2 \sigma(I)$ ] | $R1 = 0.0495$ , $wR2 = 0.1125$                                 |
| Absolute structure parameter            | 0.48(7)  |
| Extinction coefficient                  | 0.011(1)   |
| Largest diff. peak and hole             | 0.795 and $-1.047 \text{ e} \cdot \text{\AA}^{-3}$             |

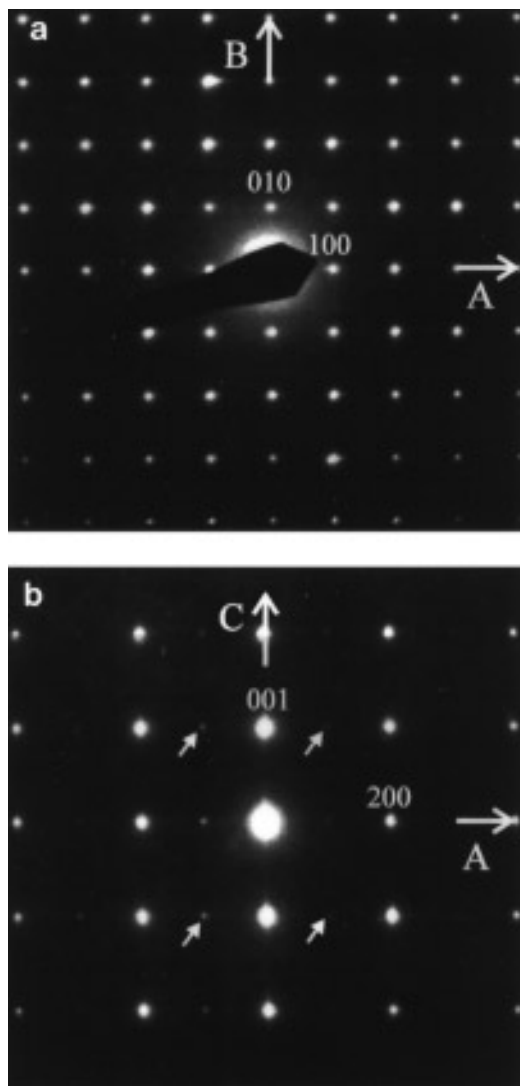


FIG. 2. Typical electron diffraction patterns of  $(\text{NH}_4)_2\text{VO}(\text{V}_{2-x}\text{P}_x\text{O}_7)$  along  $[001]$  (a) and  $[010]$  (b).

up to date all the fresnoite structures were solved in the noncentrosymmetric  $P4bm$  (No. 100) space group involving only the condition  $0kl$ ,  $k = 2n$ . In our case, this condition was not fulfilled: strong reflections occur with  $k = 2n$ , but weak ones appear with  $k = 2n + 1$ .  $\psi$  scan measurements show that they are intrinsic to the structure and don't originate from double diffraction phenomena. This is consistent with the space group  $P4$  which was used for the refinement. The real symmetry was verified by an electron diffraction study performed on a JEOL 2010 TEM fitted with a side entry goniometer ( $\pm 30^\circ$ ). Very low electron beam doses were necessary to get a series of diffraction patterns and reconstruct the reciprocal space without damaging the sample.

Specimens for electron microscopy were prepared by suspending very thin crystals in alcohol (obtained from a

TABLE 2  
Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $(\text{NH}_4)_2\text{VO}(\text{V}_{2-x}\text{P}_x\text{O}_7)$

| Atoms  | $\tau^a$ | $x$       | $y$       | $z$         | $U(\text{eq})^b$ |
|--------|----------|-----------|-----------|-------------|------------------|
| V(1)   | 0.52 (1) | 3694 (1)  | 1308 (1)  | 77 (6)      | 12 (1)           |
| P (1)  | 0.48 (1) | 3694 (1)  | 1308 (1)  | 77 (6)      | 12 (1)           |
| V (2)  | 1.0      | 5000      | 5000      | 0           | 14 (1)           |
| V (3)  | 1.0      | 0         | 0         | 86 (6)      | 15 (1)           |
| O (1A) | 1.0      | 0         | 0         | 2928 (16)   | 30 (2)           |
| O (2B) | 1.0      | 5000      | 5000      | 2802 (14)   | 28 (2)           |
| O (3B) | 1.0      | 3698 (5)  | 1302 (5)  | 2857 (8)    | 23 (1)           |
| O (4)  | 1.0      | 5000      | 0         | -922 (12)   | 44 (2)           |
| O (5)  | 1.0      | 4166 (5)  | 2987 (4)  | -991 (9)    | 26 (1)           |
| O (6)  | 1.0      | 2018 (4)  | 830 (5)   | -985 (9)    | 24 (1)           |
| N      | 1.0      | 1700 (6)  | 3308 (6)  | -4708 (11)  | 30 (1)           |
| H (1)  | 1.0      | 2388 (58) | 2704 (69) | -5472 (112) | 133 (29)         |
| H (2)  | 1.0      | 858 (50)  | 3445 (92) | -5624 (102) | 133 (29)         |
| H (3)  | 1.0      | 2135 (75) | 4234 (42) | -4394 (146) | 133 (29)         |
| H (4)  | 1.0      | 1420 (85) | 2849 (84) | -3342 (79)  | 133 (29)         |

<sup>a</sup>  $\tau$  is the occupancy factor.

<sup>b</sup>  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

thorough grinding of single crystals of the sample); few droplets of the suspension were put on a carbon coated holey film. The electron microscopy study attested the homogeneity of the samples and the electron diffraction (ED) study confirmed the crystal parameters determined by X-ray diffraction as illustrated by the two typical ED patterns along [001] and [010] (Figs. 2a and 2b).

Reconstruction of the reciprocal space allows the tetragonal cell parameters to be determined, i.e.,  $a \approx 8.6 \text{ \AA}$ ,  $c \approx 5.6 \text{ \AA}$  without any extinction conditions. Moreover, numerous ED patterns taken on different crystals evidence

TABLE 3  
Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $(\text{NH}_4)_2\text{VO}(\text{V}_{2-x}\text{P}_x\text{O}_7)$

| Atoms  | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|--------|----------|----------|----------|----------|----------|----------|
| V (1)  | 10 (1)   | 10 (1)   | 17 (1)   | 5 (1)    | 0 (1)    | -2 (1)   |
| P (1)  | 10 (1)   | 10 (1)   | 17 (1)   | 5 (1)    | 0 (1)    | -2 (1)   |
| V (2)  | 13 (1)   | 13 (1)   | 17 (1)   | 0        | 0        | 0        |
| V (3)  | 13 (1)   | 13 (1)   | 19 (1)   | 0        | 0        | 0        |
| O (1A) | 33 (3)   | 33 (3)   | 23 (4)   | 0        | 0        | 0        |
| O (2B) | 31 (2)   | 31 (2)   | 21 (4)   | 0        | 0        | 0        |
| O (3B) | 24 (2)   | 24 (2)   | 20 (2)   | 1 (1)    | 2 (1)    | 4 (1)    |
| O (4)  | 32 (3)   | 82 (6)   | 18 (2)   | 0        | 0        | -12 (3)  |
| O (5)  | 31 (2)   | 12 (1)   | 35 (2)   | 0 (1)    | -11 (2)  | -4 (1)   |
| O (6)  | 14 (1)   | 27 (2)   | 31 (2)   | 4 (2)    | 0 (1)    | -7 (1)   |
| N      | 34 (2)   | 38 (2)   | 18 (2)   | 0 (2)    | 0 (2)    | 18 (2)   |

Note. The anisotropic displacement factor exponent takes the form  $-2\pi^2 [h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$ .

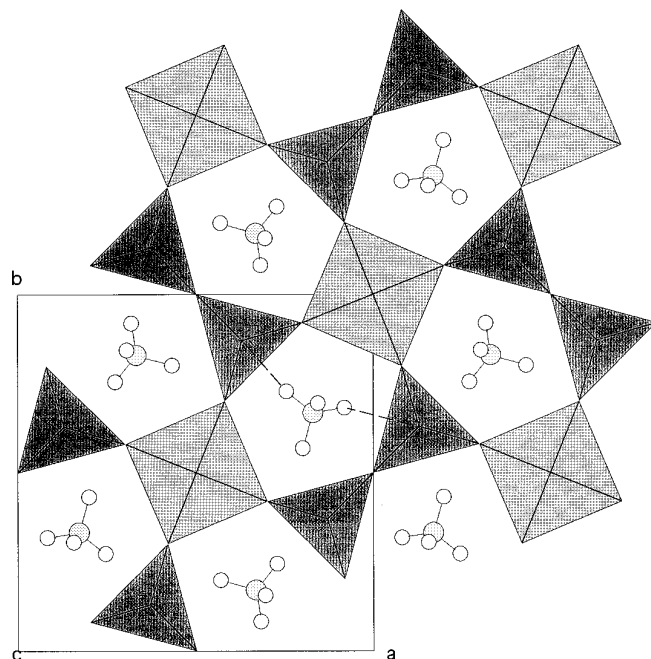


FIG. 3. Projection of  $(\text{NH}_4)_2\text{VO}(\text{V}_{2-x}\text{P}_x\text{O}_7)$  along [001] (broken lines for strongest hydrogen bonds).

the presence of very weak reflections  $0kl$ ,  $k \neq 2n$  (arrows Fig. 2b) as in the X-ray diffraction study, leading to the choice of the  $P4$  group instead of  $P4bm$  to solve the structure. Unfortunately, the weak stability of the samples under the electron beam did not allow a high resolution study with our 200 KV electron microscope.

The crystal structure was solved by direct methods using

TABLE 4  
Principal Bond Lengths ( $\text{\AA}$ ) and Angles ( $^\circ$ ) in  $(\text{NH}_4)_2\text{V}^{\text{IV}}\text{O}(\text{V}_{2-x}\text{P}_x\text{O}_7)$

| V(1)                                 | (PV(1)O <sub>4</sub> tetrahedron) |           |           |           |
|--------------------------------------|-----------------------------------|-----------|-----------|-----------|
|                                      | O(3)                              | O(6)      | O(5)      | O(4)      |
| O(3)                                 | 1.570 (6)                         | 2.641 (7) | 2.646 (7) | 2.661 (7) |
| O(6)                                 | 111.8 (3)                         | 1.619 (4) | 2.627 (6) | 2.671 (4) |
| O(5)                                 | 112.0 (3)                         | 108.3 (3) | 1.621 (4) | 2.676 (4) |
| O(4)                                 | 109.3 (3)                         | 107.5 (2) | 107.7 (2) | 1.692 (3) |
| V(2,3)O <sub>5</sub> square pyramids |                                   |           |           |           |
| V(2)-O(2)                            |                                   | 1.583 (8) |           | Apical    |
| V(2)-O(5)                            |                                   | 1.962 (4) |           | (4 ×)     |
| O(2)-V(2)-O(5)                       |                                   | 106.6 (2) |           | (4 ×)     |
| O(5)-V(2)-O(5)                       |                                   | 85.33 (8) |           | (4 ×)     |
| O(5)-V(2)-O(5)                       |                                   | 146.8 (3) |           | (2 ×)     |
| V(3)-O(1)                            |                                   | 1.61 (1)  |           | Apical    |
| V(3)-O(6)                            |                                   | 1.978 (4) |           | (4 ×)     |
| O(1)-V(3)-O(6)                       |                                   | 107.8 (2) |           | (4 ×)     |
| O(6)-V(3)-O(6)                       |                                   | 84.6 (1)  |           | (4 ×)     |
| O(6)-V(3)-O(6)                       |                                   | 144.4 (3) |           | (2 ×)     |

TABLE 5  
[P, V]–O Distances (Å) in  $(\text{NH}_4)_2\text{V}^{\text{IV}}\text{O}(\text{V}_{2-x}^{\text{V}}\text{P}_x\text{O}_7)$

|                   | $(\text{NH}_4)_2\text{VO}(\text{V}_2\text{O}_7)$ | $(\text{NH}_4)_2\text{VO}(\text{V}_{2-x}\text{P}_x\text{O}_7)$ | $\text{K}_2\text{VO}(\text{P}_2\text{O}_7)$ |
|-------------------|--|--|---|
| [P, V]–O apical   | 1.660 (5)  | 1.570 (6)  | 1.491 (6)                                   |
| [P, V]–O bridging | 1.793 (2)  | 1.692 (3)  | 1.611 (3)                                   |
| [P, V]–O          | 1.709 (3) (2×)                                   | 1.619 (4)<br>1.621 (4)   | 1.524 (4) (2 ×)                             |

the SHELXS-86 program (option TREF) (13). Vanadium atoms were first located. The positions of remaining atoms, including hydrogen, were deduced from Fourier-difference syntheses using SHELXL-93 (14). In the final stage, the occupation of the disordered  $\text{V}^{\text{V}}\text{–P}$  (4d) crystallographic site was refined to 48(1)% for phosphorus. The final reliability factors  $R1(F_0)$  and  $wR2(F_0^2)$  defined in (14) were, respectively, 0.0495 and 0.1125 for 1747 independent reflections. The atomic coordinates and the anisotropic thermal motions are listed in Tables 2 and 3.

An occupation factor of nearly 0.5 lead us to imagine an ordered arrangement of V and P in the tetrahedral sites. This hypothesis requires a lower symmetry. All our attempts of refinement in the subgroups of  $P4$  allowing this cationic order failed, thus confirming the statistical distribution.

## DISCUSSION

$(\text{NH}_4)_2\text{VO}(\text{V}_{2-x}\text{P}_x\text{O}_7)$  presents the two-dimensional fresnoite type (Fig. 3) with the ammonium cations intercalated between the inorganic layers stacked along [001]. The  $\text{V}^{\text{IV}}$  atoms are distributed on two (1a) and (1b) crystallographic sites whereas they were located on a single site in the description using the  $P4bm$  symmetry. Their coordination is square pyramidal (Table 4); they share four corners with four different  $(\text{V}(1), \text{P})\text{O}_4$  tetrahedra and their apical oxygen points toward the interlayer space. The equatorial distances are longer than the apical with numerical values exactly similar to those encountered in  $(\text{NH}_4)_2\text{VO}(\text{V}_2\text{O}_7)$  (7).

The tetrahedral site is filled by the  $\text{V}^{\text{V}}$  and P atoms statistically distributed. Each tetrahedron is linked to two square pyramids (one  $\text{V}(2)\text{O}_5$  via O(5) and one  $\text{V}(3)\text{O}_5$  via O(6)) and to one tetrahedron via O(4), the fourth vertex O(3) being free. As in the other fresnoite compounds, one observes a large distribution of distances related to the nature of the neighbors of each oxygen of the tetrahedron. In agreement with bond valence considerations (15), the  $M^{\text{V}}\text{–O}(4)$  distance (1.692(3) Å) is longer since O(4) is bonded to two pentavalent elements;  $M^{\text{V}}\text{–O}(3)$  (1.570(6) Å) is the shorter distance since O(3) is terminal. The two medium distances (1.619(4) and 1.621(4) Å) correspond to oxygens bridging  $\text{V}^{\text{IV}}$  and  $M^{\text{V}}$ . However,

these distances are not convenient with V–O or P–O bond lengths. Table 5, indicating the three kinds of distances encountered in  $(\text{NH}_4)_2\text{VO}(\text{V}_2\text{O}_7)$  (7),  $\text{K}_2\text{VO}(\text{P}_2\text{O}_7)$  (10), and our compound, shows that the distances observed in  $(\text{NH}_4)_2\text{VO}(\text{V}_{2-x}\text{P}_x\text{O}_7)$  are exactly median between the two others in respect to the statistic occupation of the site by  $\text{V}^{\text{V}}$  and P atoms.

In the inorganic layers, all the free apices (O(3) for the tetrahedra, O(1) and O(2) for the square pyramids) point on the same side of the layer but only the free apices of the tetrahedra give strong hydrogen bonds with the ammonium cations (O(3)–H(1) 1.91(6) Å, and O(3)–H(2) 2.06(5) Å) (Fig. 3).

## CONCLUSION

In this work, we have evidenced for the first time the possibility of  $\text{V}^{\text{V}}\text{–P}$  substitution in the tetrahedral subnetwork of the  $\text{A}_2\text{VOM}_2\text{O}_7$  family. In the case of ammonium compounds, “chimie douce” reactions will be performed using the method of Pouchard *et al.* (16) in order to obtain new phosphovanadates without any cationic species inserted between the planes.

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