

## Composite Microporous Compounds (MIL-*n*)

### II. Hydrothermal Synthesis and *ab Initio* Resolution by X-Ray Powder Diffraction of MIL-5: A Vanadodiphosphonate with a Three-Dimensional Neutral Framework

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Moderate heating (473 K) under hydrothermal conditions of a mixture of  $\text{NH}_4\text{VO}_3$ , ethylenediphosphonic acid, and water in the molar ratio 1:0.57:500 leads to the synthesis of a light blue powder compound formulated  $(\text{H}_2\text{O})[\text{V}_2\text{O}_2(\text{OH})\{\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_3\}]$  (labeled MIL-5). Its structure was solved *ab initio* from X-ray powder diffraction data and its symmetry is monoclinic ( $P2_1/m$  (No. 11)) with lattice parameters  $a = 7.903(1) \text{ \AA}$ ,  $b = 9.355(1) \text{ \AA}$ ,  $c = 7.485(1) \text{ \AA}$ ,  $\beta = 118.25(1)^\circ$ ,  $V = 487.42(1) \text{ \AA}^3$ , and  $Z = 2$ . The compounds neutral three-dimensional framework is built up from dimeric units of face-shared  $\text{VO}_5(\text{OH})$  octahedra linked by tetrahedral diphosphonic groups. The water molecules are inserted in the cavities of the structure. © 1998

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#### INTRODUCTION

With the aim of synthesizing some materials with open frameworks, we have focused our attention on a series of oxyfluorinated metallophosphates templated by organic cations: the ULM-*n* ( $n \leq 19$ ) compounds. Their generic chemical formula is  $M_x(\text{PO}_4)_y F_z$  (organic template) with  $M = \text{Al}$ ,  $\text{Ga}$ ,  $\text{V}$ , and  $\text{Fe}$ . In the systems containing gallium, members  $n = 5(1)$  and  $n = 16(2)$  correspond to three-dimensional frameworks with tunnels delimited by 16-membered rings. On the other hand, ULM-7 (3) is the first oxyfluorinated vanadophosphate with an open structure. Finally, ULM-3, -4, -12 and -15 (4) synthesized with iron are the first three-dimensional magnetic compounds with open frameworks, with Néel temperatures in the range 10–38 K.

In the ULM phases, the organic cation acts both as a structure-directing agent and as a counterion to the anionic framework. A consequence is the difficulty in extracting the template, its thermal degradation often leading to the collapse of the structure. To overcome this difficulty, we have recently initiated a new approach to the problem using some alkyldiphosphonic acids in the synthesis medium. This

time, instead of a templating effect, the organic part plays a space-filling role and participates in the three-dimensional framework by strong covalent linkages (P–C and C–C). The pioneering works of Clearfields ((5) and references therein) and Alberti (6) had shown the ability of phosphonic acids to give such composite materials. Using monophosphonic acids, they principally obtained lamellar compounds, but a few examples of 3D-metallodiphosphonates are also described in the literature (7).

We have recently initiated a new series labeled MIL-*n* (for Materials of Institut Lavoisier). In this series, MIL-2 and MIL-3 (8) are two three-dimensional vanadodiphosphonates which insert ammonium cations into their structure. The present work deals with the characterization of MIL-5. Its three-dimensional structure presents the special feature of being neutral, inserting solely some water molecules.

#### EXPERIMENTAL

##### Synthesis

$(\text{H}_2\text{O})[\text{V}_2\text{O}_2(\text{OH})\{\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_3\}]$  (MIL-5) was synthesized hydrothermally from  $\text{NH}_4\text{VO}_3$  (99%, Prolabo), ethylenediphosphonic acid (Alfa), and deionized water in the molar ratio 1:0.57:500. The mixture was heated at 473 K for 4 days. The initial pH was approximately 2–3 and increased to 6–7 by the end of the reaction. After filtering, a light blue powder of MIL-5 was obtained. It is worth noting that MIL-3, formulated  $(\text{NH}_4)[\text{V}^{\text{V}}\text{O}(\text{H}_2\text{O})(\text{V}^{\text{IV}}\text{O})\{\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_3\}]$  (8), is prepared in the form of green crystals by heating under hydrothermal conditions the same initial mixture 30°C lower.

##### Chemical Analysis

Thermogravimetric analysis, performed with a TA Instruments TGA 2050 apparatus under an oxygen flow, shows a single large weight loss in the range 100–250°C, corresponding to the loss of water molecules. The measured

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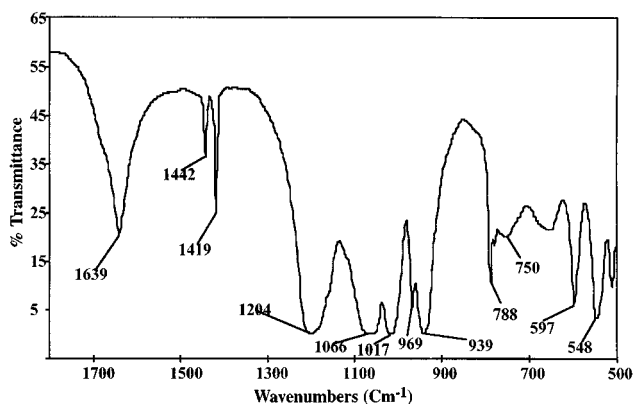


FIG. 1. IR spectrum of the MIL-5 compound.

weight loss (10.5%) is in good agreement with the theoretical weight loss (9.9%). The density of the powder was measured with a Micromeritics multipycnometer under a He flow. Elemental analysis leads to a V/P ratio equal to 0.97 (theoretical = 1) but also shows the absence of ammonium cations in the final product ( $N_{\text{total}} < 0.05\%$ ). The IR spectrum (Fig. 1), recorded on a Nicolet Magna-IR 550 in the range 2000–300  $\text{cm}^{-1}$ , confirms unambiguously the absence of  $\text{NH}_4^+$  cations (no large band around 1400  $\text{cm}^{-1}$ ). The two bands located around 1400  $\text{cm}^{-1}$  concern  $\text{CH}_2$  vibrators and those around 1200, 970, and 750  $\text{cm}^{-1}$

correspond to  $\text{PO}_3$ ,  $\nu(\text{V}=\text{O}_{\text{terminal}})$ , and  $\nu(\text{V}-\text{O}_{\text{bridging}})$ , respectively.

#### X-Ray Powder Diffraction

The MIL-5 powder was first ground in acetone with a McCrone apparatus to homogenize the grain size and then introduced vertically in a McMurdie sample holder to limit the preferential orientation effects. The diffraction pattern was collected on a Siemens D5000 diffractometer equipped with a secondary monochromator. The pattern was indexed with the Dicvol91 program (9), and a monoclinic solution was found with satisfactory figures of merit ( $M/F(2\theta) = 24/29.4$  (0.0134, 38)). The systematic absence ( $0k0$ ,  $k = 2n + 1$ ) was consistent with the centrosymmetric space group  $P2_1/m$  (No. 11). The pattern matching was adjusted with Fullprof 97 (10) and the structure was then solved by a direct method using Sirpow92 (11). Distance and angular constraints were applied during the refinement performed with Fullprof: mean distances  $\text{V}-\text{O} = 2 \text{ \AA}$ ,  $\text{P}-\text{O} = 1.55 \text{ \AA}$ ,  $\text{P}-\text{C} = 1.8 \text{ \AA}$ , and  $\text{C}-\text{C} = 1.5 \text{ \AA}$ . An overall thermal factor applied to all atoms was refined. The final agreement factors (12,13) are quite satisfactory:  $R_p = 11.3\%$ ,  $R_{\text{wp}} = 14.9\%$  (nonconventional Rietveld factors),  $R_{\text{Bragg}} = 10.3\%$ , and  $R_F = 8\%$ ; the corresponding Rietveld plot is shown in Fig. 2.

The conditions of data measurement and structure refinement are summarized in Table 1. The  $d$ -spacings are given in

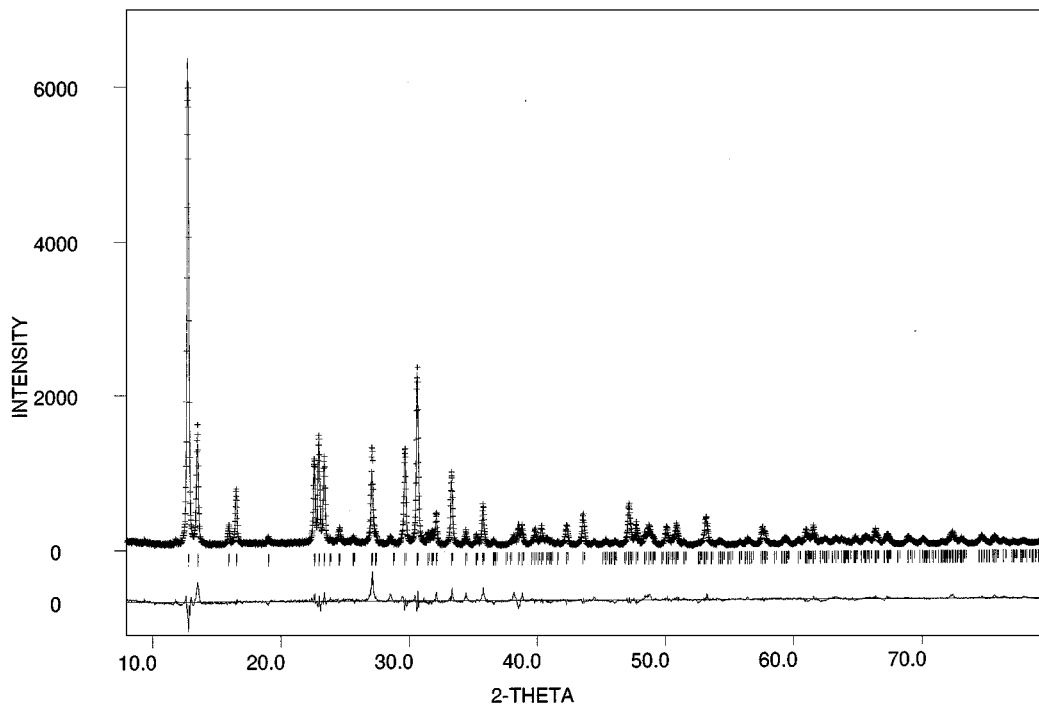


FIG. 2. Final Rietveld plot of the structure refinement of MIL-5.

**TABLE 1**  
**Crystallographic Data for (H<sub>2</sub>O)[V<sub>2</sub>O<sub>2</sub>(OH){O<sub>3</sub>P(CH<sub>2</sub>)<sub>2</sub>PO<sub>3</sub>}]**  
**(MIL-5)**

Formula weight (g·mol <sup>-1</sup> )	355
Calculated/measured density (g·cm <sup>-3</sup> )	2.420/2.15(2)
Crystal System	Monoclinic
Space Group	<i>P</i> 2 <sub>1</sub> / <i>m</i> (No. 11)
Lattice parameters	<i>a</i> = 7.903(1) Å <i>b</i> = 9.355(1) Å <i>c</i> = 7.485(1) Å <i>β</i> = 118.25(1)° <i>V</i> = 487.42(1) Å <sup>3</sup> <i>Z</i> = 2
Radiation (λCu (Å)): <i>Kα</i> <sub>1</sub> , <i>Kα</i> <sub>2</sub>	1.54059, 1.54439
Data collection	0 ≤ <i>h</i> ≤ 6, 0 ≤ <i>k</i> ≤ 7, -6 ≤ <i>l</i> ≤ 6
Pattern range (deg 2θ)	8–80
Step size (deg)	0.02
Number of reflections	646
Number of profile points	3601
Number of refined parameters	44
Number of refined atoms	11
<i>R</i> <sub>p</sub> (%)	11.6
<i>R</i> <sub>wp</sub> (%)	15.2
<i>R</i> <sub>Bragg</sub> (%)	10.87
<i>R</i> <sub>F</sub> (%)	7.76

Table 2. The atomic coordinates and the principal bond distances and angles are given in Tables 3a and 3b, respectively.

The thermodiffraction study was realized on a Siemens D5000 powder diffractometer using the Co*Kα* radiation (λ = 1.7809 Å) and equipped with an Anton Parr furnace. The heating rate was 1°C/min with a step of 20°C between 200 and 500°C, and 10°C under 200°C.

## DESCRIPTION

(H<sub>2</sub>O)[V<sub>2</sub>O<sub>2</sub>(OH){O<sub>3</sub>P(CH<sub>2</sub>)<sub>2</sub>PO<sub>3</sub>}] (MIL-5) can be easily described as a pillared structure. Effectively, its three-

**TABLE 2**  
**Indexed Powder Pattern of (H<sub>2</sub>O)[V<sub>2</sub>O<sub>2</sub>(OH){O<sub>3</sub>P(CH<sub>2</sub>)<sub>2</sub>PO<sub>3</sub>}]**  
**(MIL-5) (Reflections with *I* > 5%)**

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> <sub>obs</sub> (Å)	Intensity (%)	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> <sub>obs</sub> (Å)	Intensity (%)
1	0	0	6.9517	100	2	2	-1	3.0110	12
0	0	1	6.5834	20	1	2	-2	2.9181	41
0	1	1	5.3815	7	2	2	0	2.7885	6
1	0	1	3.9390	12	0	2	2	2.6907	5
2	0	-1	3.9387	7	2	2	-2	2.6906	11
1	2	0	3.8770	22	2	1	1	2.5106	6
0	2	1	3.8094	13	0	4	0	2.3354	6
1	2	-1	3.8092	5	3	2	0	2.0760	9
0	0	2	3.2918	14	2	0	-4	1.9048	5
2	0	-2	3.2916	10	3	3	0	1.8687	6
1	2	1	3.0112	12	4	4	-2	1.5057	5

Note. The indexing is based on a monoclinic cell with dimensions *a* = 7.903(1) Å, *b* = 9.355(1) Å, *c* = 7.485(1) Å, *β* = 118.25(1).

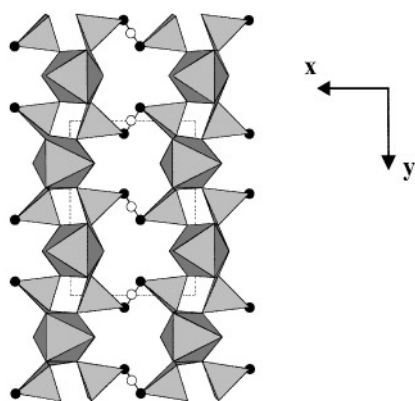
**TABLE 3**  
**(a) Atomic Coordinates (×10<sup>4</sup>) for (H<sub>2</sub>O)[V<sub>2</sub>O<sub>2</sub>(OH){O<sub>3</sub>P(CH<sub>2</sub>)<sub>2</sub>PO<sub>3</sub>}]**  
**(MIL-5)**

Atom	<i>x</i>	<i>y</i>	<i>z</i>
V(1)	382(12)	2500	5660(13)
V(2)	51(12)	2500	9608(12)
P	1918(8)	160(6)	3683(15)
O(1)	8020(29)	2500	9450(42)
O(2)	1857(35)	1115(18)	1888(24)
O(3)	9345(17)	1114(11)	7051(24)
O(4)	1420(34)	928(19)	5086(31)
O(5)	2715(19)	2500	8959(32)
O(6)	8214(26)	2500	3708(29)
C	4283(22)	-719(15)	4605(34)
Ow	5000	0000	0000

**(b) Interatomic Distances (Å) and Angles (Deg) in**  
**(H<sub>2</sub>O)[V<sub>2</sub>O<sub>2</sub>(OH){O<sub>3</sub>P(CH<sub>2</sub>)<sub>2</sub>PO<sub>3</sub>}]**  
**(MIL-5)**

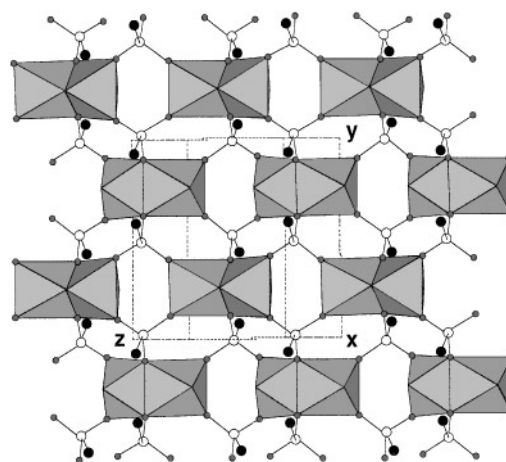
V(1)–O(6)	1.64(2)	V(2)–O(1)	1.55(3)
V(1)–O(4)	1.83(2) (2 ×)	V(2)–O(2)	2.08(2) (2 ×)
V(1)–O(3)	2.06(2) (2 ×)	V(2)–O(3)	2.15(2) (2 ×)
V(1)–O(5)	2.28(2)	V(2)–O(5)	2.37(2)
O(3)–V(1)–O(3)	78.0(1)	O(1)–V(2)–O(2)	110.2(2) (2 ×)
O(4)–V(1)–O(4)	106.8(2)	O(2)–V(2)–O(3)	153.2(1) (2 ×)
O(3)–V(1)–O(4)	86.7(1) (2 ×)	O(1)–V(2)–O(3)	96.2(2) (2 ×)
O(3)–V(1)–O(4)	162.4(2) (2 ×)	O(2)–V(2)–O(5)	80.6(1) (2 ×)
O(4)–V(1)–O(5)	91.8(1) (2 ×)	O(1)–V(2)–O(5)	165.8(2)
O(4)–V(1)–O(6)	100.7(2) (2 ×)	O(3)–V(2)–O(3)	74.0(1)
O(3)–V(1)–O(5)	76.3(1) (2 ×)	O(2)–V(2)–O(2)	77.1(1)
O(5)–V(1)–O(6)	158.8(2)	O(3)–V(2)–O(5)	72.5(1) (2 ×)
O(3)–V(1)–O(6)	87.3(1) (2 ×)	O(2)–V(2)–O(3)	98.2(1) (2 ×)
P–O(4)	1.47(2)		
P–O(3)	1.48(1)		
P–O(2)	1.59(2)		
P–C	1.85(2)		
C–C	1.68(2)		
O(2)–P–O(3)	113.0(2)		
O(3)–P–O(4)	107.2(2)		
O(2)–P–O(4)	114.6(2)		
O(3)–P–C	99.5(2)		
O(2)–P–C	100.7(2)		
O(4)–P–C	121.0(2)		
P–C–C	99.7(2)		

dimensional framework consists in the stacking along [100] of V–P–O layers strongly related by the organic ethyl chains (Fig. 3). The inorganic layers are built up from octahedral dimers connected by PO<sub>3</sub>C tetrahedral units (Fig. 4). The dimers are formed by the face-sharing of two VO<sub>5</sub>(OH) octahedra. According to valence bond calculations with the empirical data of Brese and O'Keeffe (14), it is shown that V(1) and V(2) are in the oxidation states +5 and +4, respectively; furthermore, O(5) corresponds to a hydroxyl group. The common face is described by twice the oxygen atom O(3) and the hydroxyl group, each O(3) also being



**FIG. 3.** Projection of the structure of MIL-5 along [001] showing the stacking of the V-P-O layers (black and white circles correspond to carbon and oxygen atoms, respectively).

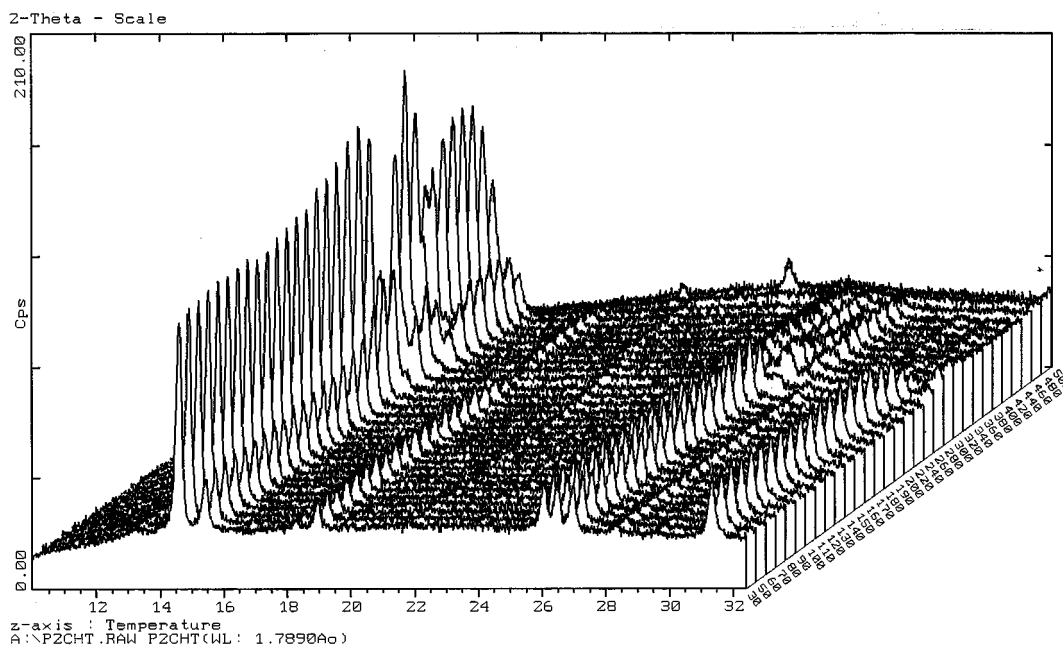
linked to one phosphorus atom. Each octahedron presents a terminal oxygen atom giving a short V=O distance ( $\approx 1.60 \text{ \AA}$ ). These two terminal apices are on the same side of the dimer but alternate up and down along the [010] direction. Some water molecules are inserted in the cavities of the structure in strong interaction with the hydroxyl groups since each water molecule possesses in its vicinity two OH groups ( $\text{Ow-O}(5) = 2.83(1) \text{ \AA}$ ) and vice versa. It is worth noting that MIL-5 is closely related to the vanadyl vanadate layers that we have recently described (15). The  $\text{V}_2\text{O}_8(\text{OH})$  octahedral dimers are substituted by  $\text{V}_2\text{O}_8$  dimers of edge-shared square pyramids, the tetrahedral groups are



**FIG. 4.** Inorganic layers of MIL-5 with ball- and 2-stick representation for the phosphonate groups (black and white circles correspond to carbon and phosphorus atoms, respectively, and small circles correspond to oxygen atoms).

constituted by vanadate units, and the interlayer spacing is occupied by diprotonated diamines.

The thermal stability of MIL-5 was estimated by both thermodiffractometric studies (Fig. 5) and TGA measurements. The structure is almost stable up to  $300^\circ\text{C}$ ; after that the dehydroxylation keeps a good crystallinity for the product. After  $400^\circ\text{C}$ , the degradation of the alkyl chain leads to the amorphization of the product. At higher temperature, recrystallization of  $(\text{VO})_2\text{P}_2\text{O}_7$  is observed.



**FIG. 5.** Thermodiffractometric measurements showing the thermal stability of MIL-5.

## ACKNOWLEDGMENT

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