JOURNAL OF SOLID STATE CHEMISTRY 111, 422–426 (1994)

Oxyfluorinated Microporous Compounds

VIII. Synthesis and Structure Determination of V_2PO_8F, *en* (ULM-7V): The First Oxyfluorovanado(V) Phosphate Templated by Ethylenediamine

Didier Riou and Gérard Férey

Laboratoire des Fluorures, URA CNRS 449, Faculté des Sciences, Université du Maine, Avenue Olivier Messiaen, 72017 Le Mans Cedex, France

Received July 16, 1993; accepted November 5, 1993

This paper describes the synthesis and the structure determination of $[V_2PO_8F]^{2-}$, $[C_2N_2H_{10}]^{2+}$(*en*), the first oxyfluorinated vanadophosphate with an open framework structure. V_2PO_8F, *en* crystallizes in the acentric $P2_12_12_1$ (No. 19) space group with cell parameters $a = 8.2939(6)$ Å, $b = 9.2260(8)$ Å, $c = 12.5021(8)$ Å $V = 956.7(2)$ Å^3, $Z = 4$. The structure consists of chains of alternating VO_6 octahedra and PO_4 tetrahedra in the [001] direction. These chains, located at $y \approx 0$ and $\frac{1}{2}$, are linked by VO_5 square pyramids at $y \approx \pm\frac{1}{4}$ levels in such a way that the two types of corner-sharing vanadium polyhedra form zigzag chains along the [100] direction. This framework defines 10-membered windows in the (110) and (1 − 10) planes and 10-membered zigzag tunnels along [001] inside which the diprotonated ethylenediamine is located.

INTRODUCTION

Numerous studies have investigated the microporous frameworks derived from the $AlPO_4$ and $GaPO_4$ families due to their potential as catalysts or molecular sieves. In these zeolite frameworks, the coordination around Al and Ga atoms is always tetrahedral. However, in the recently synthesized microporous oxyfluorinated alumino- or gallophosphates labeled ULM-*n* (1, 5), Al or Ga, display more varied coordinations: trigonal bipyramid in $Ga_4P_3O_{12}F_2(OH)_2(H_2O)_2$, 0.5 DABCO (1) and octahedral in $Ga_3(PO_4)(HPO_4)_2F_3(OH)$, $C_6N_2H_{14}$, $0.5H_2O$ (2), for example. Such coordinations are very often encountered around the 3*d* transition metals; nevertheless a few examples of a *total* substitution of Al or Ga atoms by a 3*d* transition element have been documented. Exceptions are the phosphonate compounds $(VO_2)(CH_2(PO_3)_2)$, $4H_2O$ (6), $VOC_6H_5PO_3$, H_2O (7), and vanadophosphates $[(CH_3)_2NH_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7]$, $4H_2O(H_3NCH_2CH_2NH_3)(H_3NCH_2CH_2NH_2)[V(H_2O)_2(VO)_8(OH)_4(HPO_4)_4(PO_4)_4(H_2O)_2]$, $2H_2O$, very recently studied by Soghomonian *et al.* (8, 9).

In an effort to synthesize microporous vanadophosphates in fluorinated medium, we have investigated the system V_2O_5–P_2O_5–HF–ethylenediamine (denoted *en* in the following). This paper describes the synthesis and the structure determination of the first oxyfluorinated vanado(V)phosphate with a microporous framework.

EXPERIMENTAL

Sample Preparation

The title compound was prepared hydrothermally from a mixture of V_2O_5–P_2O_5–HF–*en*–H_2O in the molar ratio 1 : 1 : 2 : 1 : 80 heated for 24 hr at 453 K and cooled for 24

TABLE 1
X-Ray Powder Pattern of V_2PO_8F,*en*

h	*k*	*l*	d_{obs}	d_{cal}	I_{calc}
0	1	1	7.40	7.42	56
0	0	2	6.252	6.251	22
1	1	0	6.197	6.168	100
1	1	1	5.521	5.531	16
0	1	2	5.176	5.175	4
1	1	2	4.401	4.391	5
0	2	1	4.330	4.328	22
2	0	0	4.145	4.147	11
0	1	3	3.808	3.798	14
0	2	2	3.710	3.712	13
2	1	1	3.630	3.620	34
2	0	2 +113	3.450	3.454	15
1	2	2	3.386	3.388	8
2	1	2	3.234	3.236	5
0	2	3	3.133	3.092	7
2	2	0	3.086	3.084	41
2	2	1	2.9879	2.9942	9
1	2	3	2.9014	2.8975	7
1	1	4	2.7910	2.7880	30
2	2	3	2.4787	2.4790	5
3	3	0	2.0548	2.0560	9

0022-4596/94 $6.00

TABLE 2
Crystallographic Data and Conditions of Collection for V_2PO_8F,*en*

Determination of cell parameters	34 reflections at $2\theta \approx 30°$
Space group	$P2_12_12_1$ (No. 19)
Cell dimensions	a = 8.2939(6) Å
	b = 9.2260(8) Å
	c = 12.5021(8) Å
Volume/Z	956.7(2) Å^3/Z = 4
Crystal dimensions	0.057 × 0.065 × 0.304 mm
Crystal delimiting faces	{011}, {0 − 11}, {100}
Wavelength/monochromator	0.71069 Å (Mo$K\alpha$)/graphite
Temperature	293 K
Scan mode	ω–2θ
Step scan	$37 \le N \le 42$, every 0.035° and 4 sec
Aperture	3.5 × 3.5 mm^2
Absorption coefficient	μ_l = 22.87 cm^{-1}
Angular range of data collection	$2\theta \le 60°$
Range of measured h, k, l	$0 \le h \le 11$, $0 \le k \le 12$, $0 \le l \le 17$
Standard reflections (3)	3 3 4, 3 3 −4, −3, 3 4
Interval between measurements	60 min
Maximum intensity variation	0.5%
Measured diffractions	1641
Independent reflections	1105
$\lvert F\rvert > 6\sigma\lvert F\rvert$	
Weight	$1/(\sigma^2(F) + F^2)$
Number of refined parameters	158
Final Fourier residuals	−0.41 to 0.45 $e \cdot$ Å^{-3}
R_w/R	0.026/0.026
R_w/R enantiomorph	0.029/0.029

TABLE 3
Atomic Positions (×10^4) and B_{eq} (Å^2) in V_2PO_8F,*en*

	x	y	z	B_{eq}
V(1)	7460(1)	640(1)	3949(1)	1.10(3)
V(2)	4765(1)	7907(1)	4972(1)	0.97(2)
P	7414(2)	671(2)	1359(1)	0.75(4)
O(1)	7655(5)	553(4)	5535(3)	1.2(1)
O(2)	9001(5)	8274(5)	6200(3)	1.3(2)
O(3)	7661(6)	29(4)	7464(3)	1.2(1)
O(4)	5974(5)	8501(5)	6271(35)	1.3(2)
O(5)	849(5)	6681(5)	1223(3)	1.4(2)
O(6)	3948(6)	6837(5)	1054(4)	1.9(2)
O(7)	1127(5)	6235(5)	5789(3)	1.6(2)
O(8)	8258(5)	6002(4)	4888(4)	2.1(2)
F	4465(4)	6201(4)	5834(3)	1.6(1)
N(1)	6187(5)	5717(5)	7715(4)	1.4(2)
N(2)	7467(7)	3435(5)	6130(3)	1.6(2)
C(1)	7892(7)	3581(6)	7287(5)	1.6(2)
C(2)	7870(6)	5139(6)	7657(5)	1.3(2)
H(1)	6277(5)	6626(5)	8258(4)	4.0(6)
H(2)	5411(5)	4899(5)	8059(4)	4.0(6)
H(3)	5687(5)	6078(5)	6962(4)	4.0(6)
H(4)	7805(7)	2342(5)	5912(3)	4.0(6)
H(5)	8131(7)	4198(5)	5645(3)	4.0(6)
H(6)	6189(7)	3583(5)	5999(3)	4.0(6)
H(7)	7050(7)	2898(6)	7713(5)	4.0(6)
H(8)	9084(7)	3111(6)	7331(5)	4.0(6)
H(9)	8390(6)	5940(6)	7129(5)	4.0(6)
H(10)	8371(6)	5266(6)	8451(5)	4.0(6)

Note. $B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$.

hr at room temperature in a Teflon-walled autoclave under autogenous pressure (filling rate ≈ 40%). After washing with water and drying in air, the solid phase V_2PO_8F,*en* was obtained almost pure (98%) in the form of violet crystals. Its X-ray powder pattern is given in Table 1. A few minute unknown green crystals were detected beside the title compound.

Structure Determination

The quality of the selected crystalline needle was tested on Laue photographs (selection on 15 crystals). The characteristics of the X-ray data collection, performed on a Siemens AED2 four-circle diffractometer, are summarized in Table 2. The intensities were corrected for Lo-

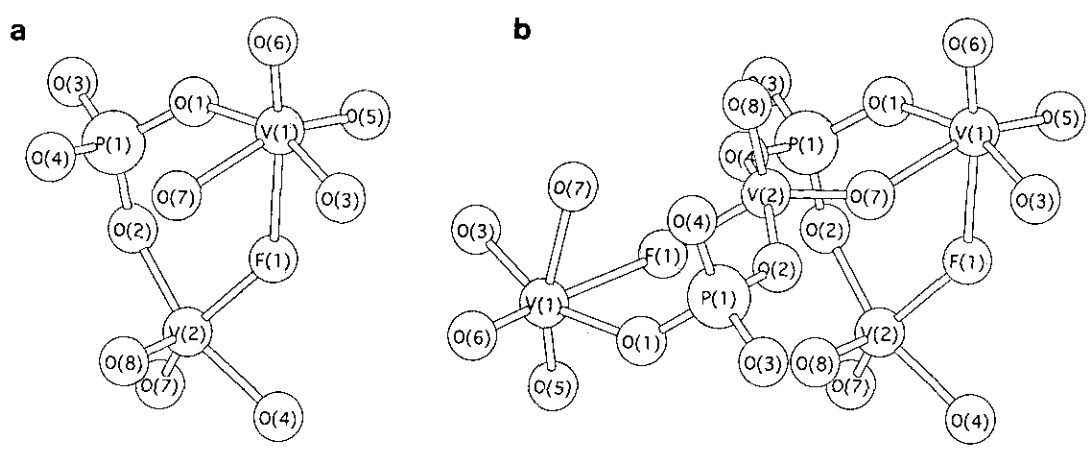

FIG. 1. (a) The asymmetric unit in V_2PO_8F,*en* and (b) the mode of connection between two of them.

TABLE 4
Interatomic Distances (Å) and Angles (°) in V_2PO_8F,en

$V(1)O_5F$ octahedron

V(1)	O(6)	O(5)	O(3)	O(1)	O(7)	F
O(6)	**1.607(5)**	2.583(7)	2.745(6)	2.668(6)	2.854(7)	3.993(6)
O(5)	102.1(2)	**1.713(4)**	2.728(6)	2.730(6)	3.718(6)	2.716(6)
O(3)	100.2(2)	95.7(2)	**1.959(4)**	3.886(5)	2.649(6)	2.968(6)
O(1)	95.1(2)	94.7(2)	159.3(2)	**1.991(4)**	2.658(6)	2.793(5)
O(7)	100.7(2)	157.1(2)	81.9(2)	81.5(2)	**2.079(5)**	2.769(5)
F	173.3(2)	81.0(2)	85.4(2)	78.6(1)	76.2(1)	**2.393(4)**

$V(2)O_4F$ square pyramid

V(2)	O(8)	O(7)	F	O(2)	O(4)
O(8)	**1.614(4)**	2.641(6)	2.911(5)	2.731(6)	2.717(6)
O(7)	106.8(2)	**1.676(4)**	3.408(6)	2.629(6)	2.590(5)
F	110.4(2)	142.4(2)	**1.924(4)**	2.616(5)	2.523(6)
O(2)	100.4(2)	93.3(2)	85.4(2)	**1.932(4)**	3.860(6)
O(4)	97.5(2)	89.6(2)	80.4(2)	160.2(2)	**1.986(4)**

PO_4 tetrahedron

P	O(1)	O(3)	O(2)	O(4)
O(1)	**1.526(4)**	2.460(5)	2.522(6)	2.484(6)
O(3)	107.2(2)	**1.530(4)**	2.521(6)	2.525(6)
O(2)	110.8(2)	110.6(2)	**1.538(5)**	2.521(6)
O(4)	108.0(2)	110.5(2)	109.8(3)	**1.544(5)**

Ethylenediamine

C(1)–C(2)	1.510(8)		
C(1)–N(2)	1.495(7)	C(2)–N(1)	1.496(7)
N(1)–H(1)	1.081(7)	N(1)–H(2)	1.081(6)
N(1)–H(3)	1.081(7)	N(2)–H(4)	1.082(7)
N(2)–H(5)	1.080(7)	N(2)–H(6)	1.081(8)
C(1)–H(7)	1.081(8)	C(1)–H(8)	1.276(8)
C(2)–H(9)	1.080(8)	C(2)–H(10)	1.081(9)

Hydrogen bonds

O(1)–H(4)	1.721(6)	O(2)–H(8)	2.004(7)
O(2)–H(9)	2.499(7)	O(4)–H(2)	1.920(6)
O(4)–H(3)	2.408(7)	O(5)–H(1)	1.729(7)
O(5)–H(6)	1.731(7)	O(7)–H(8)	2.450(7)
O(8)–H(5)	1.918(6)	F–H(3)	1.740(6)

Framework-ethylenediamine distances

C(1)–O(6)	3.065(8)	C(2)–O(8)	3.125(8)
N(1)–O(5)	2.758(7)	N(1)–F(1)	2.787(6)
N(1)–O(4)	3.000(6)	N(2)–O(5)	2.755(7)
N(2)–O(1)	2.765(6)	N(2)–O(8)	2.907(6)
N(2)–O(6)	2.985(8)		

rentzian and polarization effects. Absorption correction data based on the crystal faces do not improve the R factor for merged reflections. Buerger photographs realized on several crystals gave the conditions of existence of the reflections ($h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$) which characterize the $P2_12_12_1$ space group (No. 19). The structure was then solved using the direct method of SHELX-76 (option TANG) (10). The scattering factors, all for neutral atoms, were those given in (10) for P, O, F, N, C and from (11) for V. All the atoms, including H, appeared on Fourier difference synthesis. Distance constraints for C–H and N–H bonds were applied during the refinement. The latter, with anisotropic thermal parameters for all atoms except H, converges to $R_w = R = 0.026$. The atomic coordinates and thermal parameters are listed in Table 3 and the principal bond lengths in Table 4. The list of U_{ij} and F_o–F_c can be obtained upon request to the authors.

DESCRIPTION

In the structure of V_2PO_8F,en, there are two independent vanadium atoms presenting two different coordination geometries. Both display the usually encountered short V=O bonds. V(1) atoms are surrounded by five oxygens and one fluorine in a distorted octahedral coordination. The O(5) and O(6) atoms; in *cis* position inside their octahedron, are terminal with two short bond lengths with V(1) (1.713(6) and 1.606(7) Å, respectively). The V(1)–F linkage is weaker with a distance of 2.393(5) Å. The V(2) atom is square-pyramidally coordinated with three oxygens and one fluorine in the basal plane and one short V=O bond at the apex (V–O(8) = 1.614(4) Å). Preliminary solid-state NMR measurements with the V nucleus and valence bond analysis of the structure (12) unambigously indicate that vanadium is present only as V^V (Table 5). However, this calculation gives a low value for O(5) (1.48 instead of 2). This could be accommodated by a partial protonation of O(5). Indeed the distances between O(5) and the nitrogen atoms of the protonated amine are very short (2.76 Å) and the distance between O(5) and H(1) beard by N(1) atom is also extremely short

TABLE 5
Valence Bond Analysis for V_2PO_8F,en

	P	V(1)	V(2)	Σ (H)	Σ
O(1)	1.265	0.602	—	0.104	1.971
O(2)	1.238	—	0.706	—	1.944
O(3)	1.279	0.656	—	—	1.935
O(4)	1.218	—	0.610	—	1.828
O(5)	—	1.275	—	0.202	1.477
O(6)	—	1.698	—	—	1.698
O(7)	—	0.474	1.410	—	1.884
O(8)	—	—	1.667	—	1.667
F	—	0.158	0.561	0.109	0.828
Σ	5.000	4.863	4.954	—	—

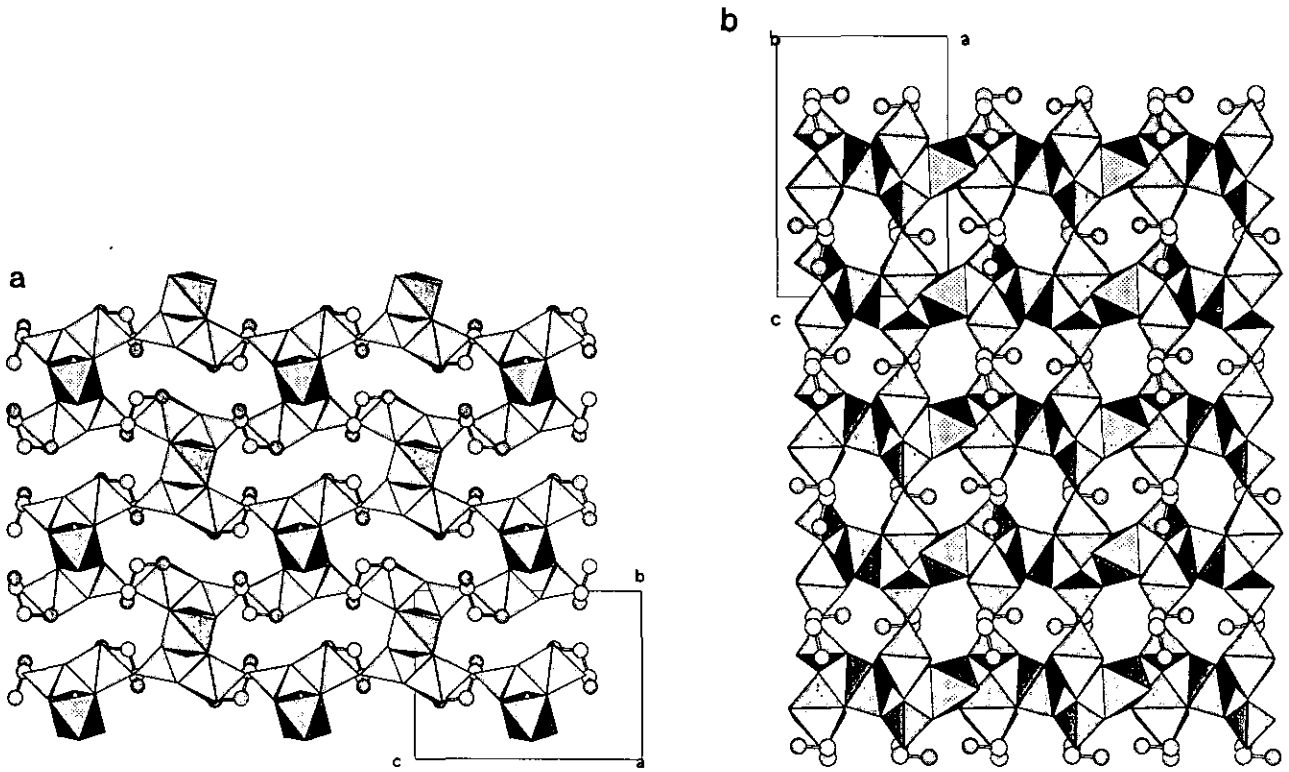

FIG. 2. (a) [100] and (b) [010] projection of V_2PO_8F,*en* showing the chains of alternate PO_4 tetrahedra and $V(1)O_5F$ octahedra running along [001].

(1.73 Å). The same situation occurs with O(5), H(6), and N(2). This might suggest in this part of the structure a delocalization of H(1) between two limits O(5)–H---N and O(5)---N–H. This means that if O(5) is protonated, one extremity of the amine becomes neutral and vice versa.

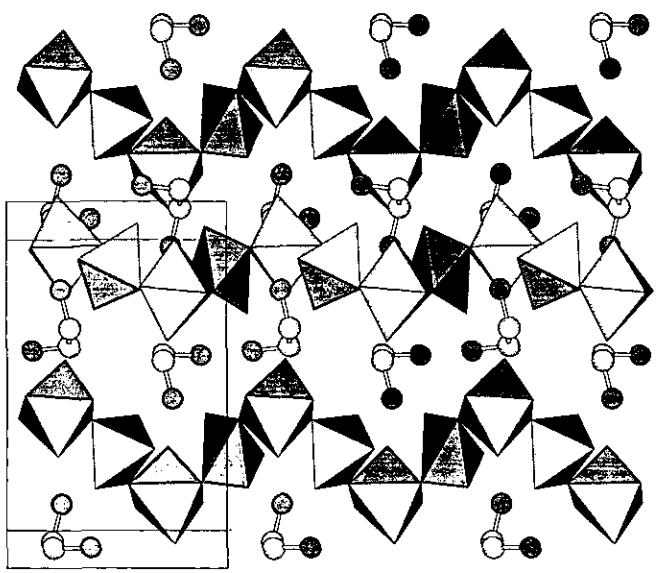

FIG. 3. Zigzag chains of alternate $V(1)O_5F$ and $V(2)O_4F$ square pyramid running along the mean direction [100].

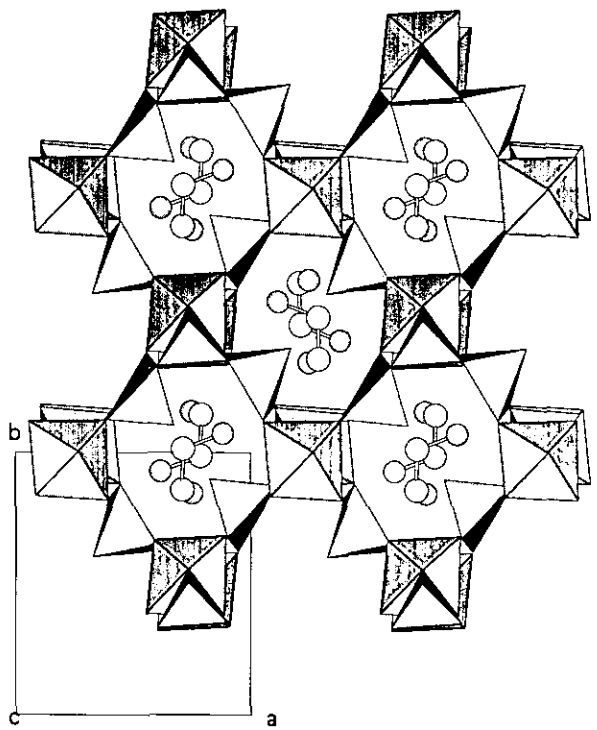

FIG. 4. View of V_2PO_8F,*en* along [001] showing the insertion of the amines in the zigzag tunnels (see text).

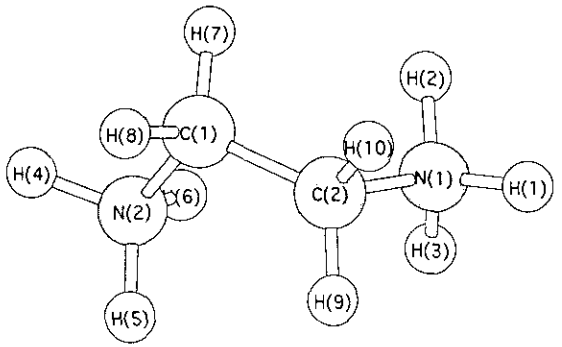

FIG. 5. Conformation of the diprotonated ethylenediamine.

The true structure is intermediate between the $[V_2PO_8F]^{-2}[C_2N_2H_{10}]^{+2}$ and $[V_2PO_8FH]^{-1}[C_2N_2H_9]^{+1}$ formulas.

The two types of vanadium(V) polyhedra are linked via the fluorine atom and each share a corner with the PO_4 tetrahedron to ensure the three-membered asymmetric unit of the structure (Fig. 1). These asymmetric units share corners in such a way that the $V(1)O_5F$ octahedra and the PO_4 tetrahedra linked by the O(1) and O(3) atoms alternating in the [001] direction form linear chains at $y \approx 0$ and $\frac{1}{2}$ levels (Fig. 2). This connection provides zigzag chains of corner-shared V(1)–V(2)–V(1) polyhedra running in the mean [100] direction (Fig. 3). This polyhedral distribution leads to the formation in the (110) and (1 −10) planes of 10-membered windows delimited by the edges of two $V(2)O_4F$ suare pyramids, four $V(1)O_5F$, and four PO_4 tetrahedra (Fig. 2). Moreover in the [001] direction some small helicoidal tunnels delimited by four chains of corner-sharing $V(1)O_5F$ octahedra and PO_4 tetrahedra and by four $V(2)O_4F$ square pyramids are formed (Fig. 4). The terminal oxygens of the vanadium polyhedra point toward the tunnels and give rise to some strong hydrogen bonds (Table 4) with the ethylenediamine located at the intersection of the tunnels. Figure 5 gives the conformation of the diprotonated ethylenediamine.

CONCLUSION

Along with vanadophosphates described in (8) and (9) V_2PO_8F,*en* provides one of the rare examples of the potential for obtaining synthetic porous phases with 3*d* transition metal elements. It is also the first case in which fluorine is present in such compounds. Moreover, it seems to be the first example of an open structure, potentially microporous, with exclusively pentavalent vanadium. However, the surprising violet color of the crystal requires further spectroscopic experimental (EPR, UV–vis, IR) investigation. These experiments are currently in progress. Some other compounds of this series will be published elsewhere (13, 14).

REFERENCES

1. Th. Loiseau and G. Férey, *Eur. J. Solid State Inorg. Chem.* **30,** 369 (1993).
2. Th. Loiseau and G. Férey, *J. Chem. Soc. Chem. Commun.*, 1197 (1992).
3. Th. Loiseau, R. Retoux, Ph. Lacorre, and G. Férey, submitted for publication.
4. Th. Loiseau, D. Riou, and G. Férey, submitted for publication.
5. Th. Loiseau and G. Férey, submitted for publication.
6. G. Huan, J. W. Johnson, A. J. Jacobson, and J. S. Merola, *J. Solid State Chem.* **89,** 220 (1990).
7. G. Huan, A. J. Jacobson, J. W. Johnson, and E. W. Corcoran, *Chem. Mater.* **2,** 91 (1990).
8. V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta, and C. J. O'Connor, *Science* **259** (1993).
9. V. Soghomonian, Q. Chen, R. C. Haushalter, and J. Zubieta, *Angew. Chem. Int. Ed. Engl.* **32**(4), 610 (1993).
10. G. M. Sheldrick, "SHELX-76, a Program for Crystal Structure Determination." University of Cambridge, 1976.
11. "International Tables for X-ray Crystallography," Vol. IV. Kynoch Press, Birmingham, 1974. [Present distributor: Kluwer Academic, Dortrecht]
12. N. E. Brese and M. O'Keeffe, *Acta Crystallogr. Sect. B* **47,** 192 (1991).
13. Th. Loiseau and G. Férey, submitted for publication.
14. D. Riou, Th. Loiseau, and G. Férey, submitted for publication.