

Hydrothermal Synthesis, Structure, and Solid State ^{19}F NMR Study of ULM-17: $(\text{H}_3\text{O})_2[\text{V}_4(\text{HPO}_4)(\text{PO}_4)_3\text{O}_6\text{F}]_2[\text{NC}_7\text{H}_{14}]_6$

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$(\text{H}_3\text{O})_2[\text{V}_4(\text{HPO}_4)(\text{PO}_4)_3\text{O}_6\text{F}]_2[\text{NC}_7\text{H}_{14}]_6$ (labeled ULM-17) has been hydrothermally synthesized (150°, 24 h, autogeneous pressure). It is monoclinic (space group $P2_1/c$ (No. 14)) with $a = 21.4747(6)$ Å, $b = 17.7223(5)$ Å, $c = 20.1616(6)$ Å, $\beta = 94.329(1)^\circ$, and $Z = 4$. The structure consists in the hexagonal close packing of discrete hydronium cations, protonated quinuclidine and molecular anions $[\text{V}_4(\text{HPO}_4)(\text{PO}_4)_3\text{O}_6\text{F}]^{4-}$ (1). The structure presents two kinds of octameric anions built up from the tetrahedral arrangement of $\text{V}^{\text{V}}\text{O}_5\text{F}$ octahedra sharing edges and vertices, capped by phosphorus tetrahedra. The stability of the solid is ensured via strong hydrogen bonds between the oxygens of the polyanions and the hydrogens of both hydronium and quinuclidinium cations. The particular location of fluorine at the center of the molecular anion 4-fold coordinated by V^{V} was studied by solid state NMR.

Introduction

Since the discovery of a new series of microporous aluminophosphates $\text{AlPO}_4\text{-}n$,¹ synthesized by using organic amines or quaternary ammonium cations as templates, numerous phosphate-based molecular sieves have been reported.^{2–4} Several years ago, Guth and Kessler⁵ developed a new route of synthesis in the presence of fluorine. The addition of this element favors mineralization and induces crystallization at neutral or acidic pH. Moreover, fluorine is often incorporated into the open frameworks. As for the LTA-type GaPO_4 ,⁶ the pure-silica octadecasil (AST),⁷ and cloverite,⁸ with 20-membered channels the fluorine is located at the center of a double four-ring (D4R) cage.

Recently,⁹ we focused attention on the hydrothermal synthesis of a new series, labeled ULM- n of fluorinated aluminophosphates in the systems M_2O_3 ($\text{M} = \text{Al}, \text{Ga}$)– P_2O_5 – HF –template– H_2O . In these phases, the situation of fluorine

is different since it is directly involved in the coordination sphere of M. We recently inferred¹⁰ that the particularly strong interaction between amino groups and fluorine is the driving force which governs by molecular recognition, the nature, and the dimensionality of the corresponding compounds. An extension of this work was to synthesize in the same way microporous compounds containing exclusively 3d transition metal cations instead of aluminium or gallium. $\text{V}^{\text{V}}\text{PO}_3\text{F}(\text{en})$ ($\text{en} = \text{ethylenediamine}$), thus isolated,¹¹ is the first oxyfluorinated microporous solid having exclusively a transition cation associated with phosphate groups as metallic species in the inorganic framework. At the same time, Haushalter et al.¹² isolated porous oxygenated mixed valence compounds. We present here our results in the system V_2O_5 – P_2O_5 – HF –quinuclidine– H_2O , corresponding to our attempts to study the influence of the nature and geometry of the amine in this new family of compounds. This leads, for large and spherical amines, to isolated heteropolyanionic species described below. This paper is devoted to ULM-17 whose chemical formula is $(\text{H}_3\text{O})_2[\text{V}_4(\text{HPO}_4)(\text{PO}_4)_3\text{O}_6\text{F}]_2[\text{NC}_7\text{H}_{14}]_6$.

Experimental Section

Synthesis. Reagent grade chemicals were used throughout. Vanadium oxide (V_2O_5 , Merck 99%+), phosphoric acid (85% H_3PO_4 , Prolabo RP Normapur), hydrofluoric acid (40% HF Prolabo RP Normapur), and quinuclidine NC_7H_{13} (Aldrich 99%+) were used as received from the commercial sources. The title compound was prepared by hydrothermal synthesis under autogeneous pressure. The starting mixture corresponding to the molar composition 1 V_2O_5 , 1 P_2O_5 , 2 HF, 1 quinuclidine, and 67 H_2O , was placed without stirring in a Teflon-lined stainless steel autoclave, was heated at 423 K for 24 h, and then was cooling to room temperature for 24 h. The acidity of the medium ($\text{pH} \approx 1\text{--}2$) is the same at the beginning and at the end of the reaction. The orange crystalline product obtained, was filtered off, washed with distilled water and dried at room temperature. Chemical

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- (1) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146.
- (2) Flanigen, E. M.; Patton, R. L.; Wilson, S. T. *Stud. Surf. Sci. Catal.* **1988**, *37*, 13.
- (3) Gier, T. E.; Stucky, G. D. *Nature* **1991**, *349*, 508.
- (4) Xu, R.; Chen, J.; Feng, C. *Stud. Surf. Sci. Catal.* **1991**, *60*, 63.
- (5) (a) Guth, J. L.; Kessler, H.; Wey, R. *Stud. Surf. Sci. Catal.* **1986**, *28*, 121. (b) Guth, J. L.; Kessler, H.; Higel, J. M.; Lamblin, J. M.; Patarin, J.; Seive, A.; Chezeau, J. M.; Wey, R. *ACS Symp. Ser.* **1989**, *398*, 176.
- (6) Kessler, H. *MRS Symp. Ser.* **1991**, *233*, 47.
- (7) Caulllet, P.; Guth, J. L.; Hazm, J.; Lamblin, J. M.; Gies, H. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 345.
- (8) Estermann, M.; McCusker, L. B.; Baerlocher, C.; Merrouche, A.; Kessler, H. *Nature* **1991**, *352*, 320.
- (9) (a) Riou, D.; Loiseau, T.; Férey, G. *J. Solid State Chem.* **1992**, *102*, 4. (b) Loiseau, T.; Férey, G. *J. Chem. Soc., Chem. Commun.* **1992**, 1197. (c) Loiseau, T.; Férey, G. *Eur. J. Solid State Inorg. Chem.* **1993**, *30*, 369. (d) Férey, G.; Loiseau, T.; Lacorre, P.; Taulelle, F. *J. Solid State Chem.* **1993**, *105*, 179. (e) Taulelle, F.; Loiseau, T.; Maquet, J.; Livage, J.; Férey, G. *J. Solid State Chem.* **1993**, *105*, 191. (f) Loiseau, T.; Lacorre, P.; Calage, Y.; Férey, G. *J. Solid State Chem.* **1993**, *105*, 417. (g) Loiseau, T.; Lacorre, P.; Retoux, R.; Férey, G. *J. Solid State Chem.* **1994**, *111*, 427. (h) Loiseau, T.; Férey, G. *J. Solid State Chem.* **1994**, *111*, 403. (i) Loiseau, T.; Riou, D.; Licheron, M.; Férey, G. *J. Solid State Chem.* **1994**, *111*, 397.

(10) Férey, G. *J. Fluorine Chem.* **1995**, *72*, 187.

(11) Riou, D.; Férey, G. *J. Solid State Chem.* **1994**, *111*, 422.

(12) (a) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Connor, J. *Science* **1993**, *259*, 1596. (b) Haushalter, R. C.; Wang, Z.; Thompson, M. E.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 3700 and references therein.

Table 1. Crystallographic Data for $(\text{H}_3\text{O})_2[\text{V}_4(\text{HPO}_4)(\text{PO}_4)_3\text{O}_6\text{F}]_2[\text{NC}_7\text{H}_{14}]_6$

$(\text{H}_3\text{O})_2[\text{V}_4(\text{HPO}_4)(\text{PO}_4)_3\text{O}_6\text{F}]_2[\text{NC}_7\text{H}_{14}]_6$	monoclinic; $P2_1/c$ (No. 14)
$a = 21.4747(6) \text{ \AA}$	$T = 20 \text{ }^\circ\text{C}$
$b = 17.7223(5) \text{ \AA}$	$\lambda (\text{MoK}\alpha) = 0.71073 \text{ \AA}$
$c = 20.1616(6) \text{ \AA}$	$\rho_{\text{obsd}} = 1.83(5) \text{ g}\cdot\text{cm}^{-3}$
$\beta = 94.329(1)^\circ$	$\rho_{\text{calcd}} = 1.834 \text{ g}\cdot\text{cm}^{-3}$
$V = 7651.2(4) \text{ \AA}^3$	$\mu = 12.70 \text{ cm}^{-1}$
$Z = 4$	$R1(F_o) = 0.0518$
$M = 2110$	$wR2(F_o^2) = 0.103$

analysis of vanadium (by manganometry) and fluorine (with a specific electrode) prove that vanadium is exclusively in the pentavalent state and that the V:F ratio is 4:1. Anal. Calcd for $(\text{H}_3\text{O})_2[\text{V}_4(\text{HPO}_4)(\text{PO}_4)_3\text{O}_6\text{F}]_2[\text{NC}_7\text{H}_{14}]_6$: V, 19.33; F, 1.80. Found: V, 19.6(1); F, 1.9(1). Thermal analysis (performed with a SETARAM TGDTA92 apparatus under O_2 flow) shows the loss of hydronium ions at $160 \text{ }^\circ\text{C}$, the organic part of the compound begins to leave the structure at $280 \text{ }^\circ\text{C}$. At $620 \text{ }^\circ\text{C}$ the resulting solid is amorphous. The proposed chemical formula was confirmed by a density measurement performed with a 1305 Micromeritics multipycnometer operating under He flow. The measured density is $1.83(5) \text{ g}\cdot\text{cm}^{-3}$ vs $1.834 \text{ g}\cdot\text{cm}^{-3}$ for the theoretical value.

Structure Determination. The quality of the parallelepipedic single crystal was tested by optical observation and Laue photographs. The intensity data collection was performed with a Siemens SMART system using a three-circle diffractometer equipped with a CCD bidimensionnal detector. A total of 32 062 intensities were measured during 5 h, the conditions of data collection are summarized in Table 1. The data were corrected for Lorentz–polarization effects, and an absorption correction based on the crystal morphology was applied. The scattering factors and anomalous dispersion corrections were taken from ref 13. The structure was solved in the $P2_1/c$ (No. 14) space group by using the direct method analysis of the SHELXTL program.¹⁴ Vanadium and phosphorus atoms were first located. The remaining atoms (anions and then N and C atoms of the amines) were found by difference Fourier maps. Refinement was performed by full-matrix least-squares analysis of SHELXL-93.¹⁵ The locations of OH groups and fluorine were deduced from (i) bond valence calculations¹⁶ and (ii) bond length considerations and then (iii) confirmed by solid state ^{19}F NMR spectroscopy. Hydrogen atoms of the organic cations were located using geometrical constraints. The refinement with anisotropic thermal parameters for all atoms except H (which were refined with a common isotropic factor) gives $R1(F_o) = 0.052$ and $wR2(F_o^2) = 0.103$ for 12 562 reflections ($I > 2\sigma(I)$) and 194 crystallographic sites. The reliability factors are defined in ref 15.

The atomic coordinates with isotropic thermal parameters are given in Table 2. H coordinates, anisotropic thermal parameters, and detailed distances and angles are given in the Supporting Information.

NMR Spectroscopy. Solid state NMR of fluorine requires high field and high spinning speed to gain resolution. The experiments were run on a ASX500 Bruker instrument for ^{19}F nucleus. A high speed probe head spinning at up to 15 kHz with 4 mm rotors has been used. NMR experimental conditions for acquisitions are reported in Table 3.

Description of the Structure

The crystal structure determination revealed the presence of discrete hydronium cations and quinuclidinium cations interleaved between two types of molecular anions $[\text{V}_4(\text{HPO}_4)(\text{PO}_4)_3\text{O}_6\text{F}]^{4-}$ (Figure 1). The later are arranged in a distorted hexagonal close packing along $[001]$.

The two crystallographically different heteropolyanions (Figures 2 and 3) are octameric with four VO_5F octahedra and four tetrahedra (one HPO_4 and three PO_4). The arrangement of the

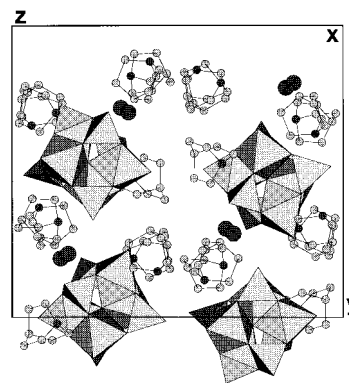


Figure 1. $[100]$ projection of the structure of $(\text{H}_3\text{O})_2[\text{V}_4(\text{HPO}_4)(\text{PO}_4)_3\text{O}_6\text{F}]_2[\text{NC}_7\text{H}_{14}]_6$ using a polyhedral model for the heteropolyanion and a balls and sticks model for quinuclidinium and hydronium cations.

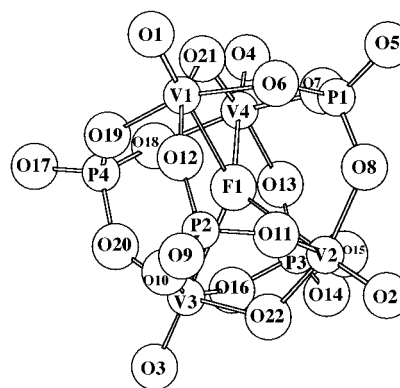
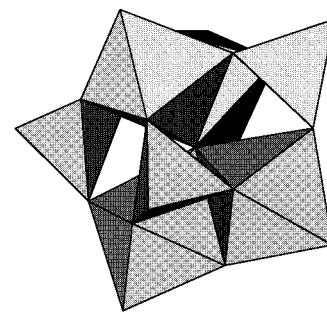


Figure 2. Bottom: View of the structure of the first molecular anion $[\text{V}_4(\text{HPO}_4)(\text{PO}_4)_3\text{O}_6\text{F}]^{4-}$ (cluster F1 in the text) showing the atom-labeling scheme. Top: Polyhedral representation of its structure.

four octahedra may be described by two orthogonal edge sharing bioctahedra sharing a vertex on which fluorine is located. The resulting tetrahedral disposition (V–V distances: $3.097\text{--}3.125 \text{ \AA}$ for the short and $4.232\text{--}4.329 \text{ \AA}$ for the long) allows the capping of each face by three oxygens of the phosphorus tetrahedra. The VO_5F octahedra are strongly distorted (see Supporting Information) with a large range of V–O, F bond distances ($1.575\text{--}2.465 \text{ \AA}$ for the cluster around F1, and $1.573\text{--}2.440 \text{ \AA}$ for the F2 cluster). All the short V=O distances (range $1.575\text{--}1.588 \text{ \AA}$ and $1.573\text{--}1.581 \text{ \AA}$ for clusters 1 and 2) point outward the cluster and are directly opposite to the long V–F bonds ($2.362\text{--}2.465 \text{ \AA}$). The latter are well explained by bond valence calculations,¹⁶ since this central fluoride ion is 4-fold coordinated to highly charged cations. It is the first time, to our knowledge, that the environment of fluorine by four pentavalent vanadium atoms is described. However, such a central position of fluorine in an heteropolyanion was recently described by Khan *et al.*;¹⁷ its distorted 6-fold coordination ($2.24\text{--}2.52 \text{ \AA}$) was ensured by V^{IV} atoms. The P–O distances (see Supporting Information) are as usual in the range 1.495--

(13) *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.

(14) Sheldrick, G. M. SHELXTL. Siemens Analytical X-ray Instruments, 1994.

(15) Sheldrick, G. M., SHELXL-93, A program for crystal structure determination. University of Göttingen, Germany, 1993.

(16) Brese, N.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for ULM-17^a

atoms	x	y	z	U(eq)	atoms	x	y	z	U(eq)
V(1)	1142(1)	124(1)	1848(1)	27(1)	O(39)*	5031(2)	3295(2)	2449(2)	51(1)
V(2)	152(1)	249(1)	3637(1)	26(1)	O(40)	4823(2)	4469(2)	1812(2)	35(1)
V(3)	1187(1)	1483(1)	3576(1)	27(1)	O(41)	4691(2)	4445(2)	3043(2)	33(1)
V(4)	1881(1)	-658(1)	3035(1)	28(1)	O(42)	3923(2)	3748(2)	2241(2)	38(1)
V(5)	3512(1)	6514(1)	1785(1)	32(1)	O(43)	3546(2)	4354(2)	3296(2)	39(1)
V(6)	4566(1)	5405(1)	1424(1)	32(1)	O(44)	4131(2)	6274(2)	1278(2)	33(1)
V(7)	4115(1)	5086(1)	3451(1)	35(1)	N(1)	3586(4)	405(4)	1239(4)	105(3)
V(8)	3177(1)	4255(1)	2463(1)	39(1)	C(1A)	3458(5)	-986(6)	907(6)	112(4)
P(1)	479(1)	-1106(1)	2690(1)	26(1)	C(1B)	2915(5)	-516(5)	705(6)	111(4)
P(2)	172(1)	1305(1)	2380(1)	27(1)	C(1C)	2956(4)	286(5)	898(5)	107(4)
P(3)	1460(1)	-12(1)	4397(1)	27(1)	C(1D)	4037(6)	-674(6)	685(5)	115(4)
P(4)	2235(1)	995(1)	2631(1)	32(1)	C(1E)	4056(4)	175(6)	814(6)	115(4)
P(5)	2838(1)	5849(1)	3001(1)	42(1)	C(1F)	3483(7)	-832(7)	1686(5)	156(6)
P(6)	4760(1)	6417(1)	2699(1)	33(1)	C(1G)	3683(5)	-109(6)	1861(4)	94(3)
P(7)	3169(1)	5009(1)	1040(1)	35(1)	N(2)	1373(2)	-3451(3)	600(2)	39(1)
P(8)	4612(1)	3987(1)	2391(1)	36(1)	C(2A)	1356(4)	-2055(4)	814(5)	73(2)
F(1)	1098(1)	280(2)	3017(1)	28(1)	C(2B)	1478(5)	-2478(5)	1466(5)	93(3)
F(2)	3834(1)	5308(2)	2286(2)	34(1)	C(2C)	1454(3)	-3335(4)	1337(3)	57(2)
O(1) ^t	1140(2)	8(2)	1069(2)	43(1)	C(2D)	734(4)	-2313(4)	493(6)	101(3)
O(2) ^t	-468(2)	206(2)	4017(2)	36(1)	C(2E)	764(3)	-3146(4)	321(4)	58(2)
O(3) ^t	1263(2)	2266(2)	3956(2)	39(1)	C(2F)	1871(4)	-2249(4)	374(4)	74(2)
O(4) ^t	2382(2)	-1308(2)	3051(2)	41(1)	C(2G)	1898(3)	-3087(4)	277(3)	52(2)
O(5)*	153(2)	-1840(2)	2440(2)	36(1)	N(3)	1408(2)	1256(2)	5823(2)	34(1)
O(6)	509(2)	-609(2)	2064(2)	27(1)	C(3A)	1237(3)	2546(3)	6295(3)	46(2)
O(7)	1133(2)	-1288(2)	3017(2)	30(1)	C(3B)	1361(3)	1993(4)	6851(3)	55(2)
O(8)	76(2)	-721(2)	3186(2)	28(1)	C(3C)	1414(3)	1197(3)	6571(3)	38(1)
O(9)	-289(2)	1871(2)	2074(2)	34(1)	C(3D)	658(3)	2296(4)	5866(3)	50(2)
O(10)	689(2)	1739(2)	2803(2)	28(1)	C(3E)	787(3)	1547(3)	5540(3)	41(2)
O(11)	-154(2)	726(2)	2810(2)	29(1)	C(3F)	1794(3)	2557(4)	5866(4)	61(2)
O(12)	477(2)	866(2)	1828(2)	28(1)	C(3G)	1927(3)	1763(3)	5633(3)	46(2)
O(13)	1847(2)	-530(2)	3970(2)	30(1)	N(4)	3316(2)	3014(3)	-1329(3)	46(1)
O(14)	1669(2)	-131(2)	5129(2)	31(1)	C(4A)	3933(4)	2550(4)	-305(4)	64(2)
O(15)	762(2)	-207(2)	4268(2)	29(1)	C(4B)	3771(4)	3368(4)	-226(4)	73(2)
O(16)	1587(2)	823(2)	4226(2)	29(1)	C(4C)	3422(4)	3659(4)	-853(4)	71(2)
O(17)	2830(2)	1358(2)	2460(2)	44(1)	C(4D)	4303(4)	2448(5)	-909(4)	82(3)
O(18)	2380(2)	219(2)	2976(2)	33(1)	C(4E)	3917(3)	2702(4)	-1526(4)	65(2)
O(19)	1768(2)	874(2)	2010(2)	31(1)	C(4F)	3326(4)	2099(4)	-415(4)	76(2)
O(20)	1921(2)	1514(2)	3125(2)	31(1)	C(4G)	2952(3)	2412(4)	-1022(4)	62(2)
O(21)	1700(2)	-564(2)	2140(2)	29(1)	N(5)	4063(3)	-1758(4)	3599(4)	89(2)
O(22)	454(2)	1137(2)	3894(2)	28(1)	C(5A)	3543(4)	-1683(7)	4691(4)	98(3)
O(23) ^t	3274(2)	7288(2)	1471(2)	46(1)	C(5B)	3614(5)	-964(6)	4380(5)	106(3)
O(24) ^t	5047(2)	5444(2)	872(2)	45(1)	C(5C)	3823(4)	-998(4)	3703(5)	77(2)
O(25) ^t	4317(2)	4955(2)	4213(2)	47(1)	C(5D)	4277(4)	-1959(7)	4797(4)	121(4)
O(26) ^t	2732(2)	3564(2)	2559(2)	52(1)	C(5E)	4573(3)	-1940(6)	4192(4)	93(3)
O(27)	2304(2)	6118(3)	3425(2)	60(1)	C(5F)	3257(4)	-2259(5)	4230(4)	81(3)
O(28)	2927(2)	6442(2)	2469(2)	37(1)	C(5G)	3607(4)	-2343(4)	3645(4)	67(2)
O(29)	2646(2)	5087(2)	2688(2)	42(1)	N(6)	-647(3)	-239(3)	1361(3)	54(2)
O(30)	3424(2)	5780(2)	3485(2)	41(1)	C(6A)	-1515(3)	-591(4)	518(4)	57(2)
O(31)	5245(2)	7024(2)	2911(2)	43(1)	C(6B)	-914(3)	-997(4)	372(3)	51(2)
O(32)	4146(2)	6816(2)	2456(2)	32(1)	C(6C)	-409(3)	-798(5)	899(4)	72(2)
O(33)	4661(2)	5931(2)	3310(2)	36(1)	C(6D)	-1669(4)	-812(5)	1219(4)	76(2)
O(34)	5014(2)	5928(2)	2149(2)	33(1)	C(6E)	-1159(4)	-567(6)	1712(4)	99(3)
O(35)	2828(2)	4846(2)	348(2)	43(1)	C(6F)	-1394(4)	260(4)	509(3)	60(2)
O(36)	2999(2)	5809(2)	1250(2)	35(1)	C(6G)	-876(4)	443(4)	1010(5)	81(3)
O(37)	3866(2)	4916(2)	952(2)	38(1)	OW1	3457(3)	1997(4)	1472(3)	116(3)
O(38)	2946(2)	4433(2)	1536(2)	38(1)	OW2	1510(3)	7156(3)	3295(5)	92(2)

^a H coordinates are given in the Supporting Information. *U*(eq) is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor. Asterisks and *t* indices for some oxygen positions correspond to O—H and V=O bonds, respectively.

Table 3. Recording Conditions for NMR Spectroscopy of ¹⁹F

standard: CFC13/0 ppm
frequency: 470.5 MHz
magnetic field: 11.7 T
pulse width: 2 μ s
dead time: 4 μ s
recycle time: 10 s
no. of scans: 32
spectral width: 250 kHz

1.561 \AA . Each tetrahedron shares three apices with three different octahedra of the same cluster, the fourth one remaining

terminal. The valence bond calculation¹⁶ gives a value around 1.25 u.v. for each unlinked oxygen and so could lead to attribute these apices to an hydroxyl group. In this case, the electro-neutrality of the compound should be ensured by the intercalation of neutral quinuclidine between $[\text{V}_4(\text{HPO}_4)_4\text{O}_6\text{F}]^-$ heteropolyanions. This fact is not consistent with the high acidity of the medium during the synthesis (pH \approx 1–2) which constrains quinuclidine (p*K*_a = 10.6) to be protonated. However, the examination of the environment around each oxygen atom, except O(5) and O(39) for the F1 and F2 clusters, respectively, shows that there is at least an ammonium or a hydronium cation in the range 2.5–3.0 \AA . These short distances are compatible with very strong hydrogen bondings between

(17) Khan, M. I.; Chen, Q.; Höpe, H.; Parkin, S.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 2929.

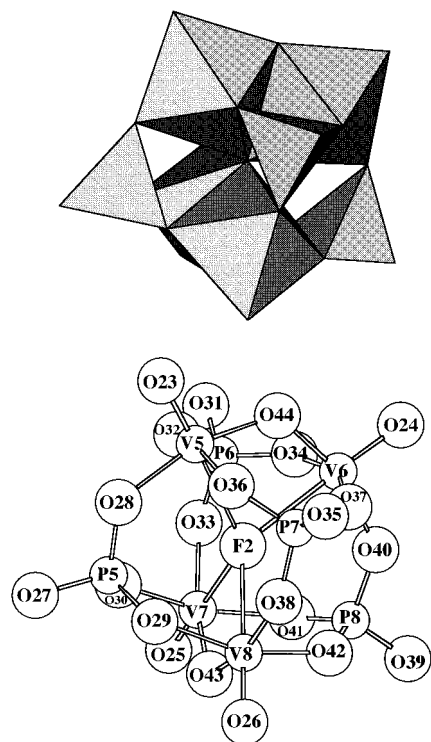


Figure 3. Bottom: View of the structure of the second molecular anion $[V_4(HPO_4)(PO_4)_3O_6F(2)]$ (cluster F2 in the text) showing the atom-labeling scheme. Top: Polyhedral representation of its structure.

the free apices of the tetrahedra and the protonated water or amine molecules. So we can suggest a model of delocalized proton between the polyanions and the inserted species.

Solid State NMR Results

The X-ray results suggest fluorines in the center of the polyanions. However, an ambiguity still prevails with atoms or groups of isoelectronic density. It is always difficult to assign definitely between a fluorine and a hydroxyl group. Fluorine NMR has been used in order to evaluate whether the assignment of fluorines is plausible or not.

The spectrum is plotted in Figure 4. Two sites are observed with isotropic chemical shifts of -178.1 and -181.8 ppm. Their anisotropies and asymmetry parameters are almost identical. They come to $+51$ ppm for the anisotropy and 0.5 for the asymmetry parameter.

The sites are only slightly different in line width with 400 Hz for the site at -181.8 ppm and 420 for the site at -178.1 ppm. A line width of less than one ppm in solid state fluorine NMR indicates a very weak dipolar or no dipolar homonuclear couplings between the fluorines. The F–F distances are therefore large, as expected with the very distant positions of the center of the polyanions (shorter F–F > 10 Å). Dipolar coupling may happen between fluorine and its first assumed neighbors: vanadiums. However distances are within 2.36 and 2.47 Å. This leads to heteronuclear dipolar coupling between

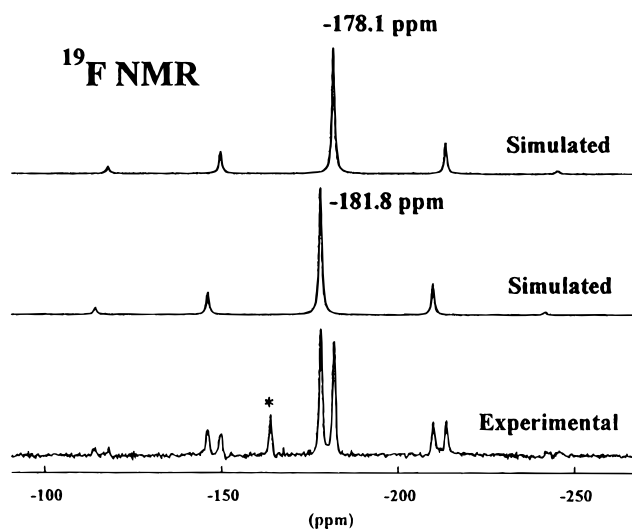


Figure 4. MAS ^{19}F NMR of $(\text{H}_3\text{O})_2[V_4(\text{HPO}_4)(\text{PO}_4)_3\text{O}_6\text{F}]_2[\text{NC}_7\text{H}_{14}]_6$. An asterisk denotes an impurity.

2.2 and 2 kHz. With a 15 kHz spinning speed, these dipolar couplings, if present, are efficiently averaged out.

The integration of two line manifolds gives a ratio of $(1.13)_{-178.1}/(1)_{-181.8}$. The population ratio is in agreement with an assignment to sites with the same occupancy.

Positions of fluorines around -180 ppm provide a hint to confirm the assignment. Actually, several fluorinated inorganic compounds have been measured.^{18,19} Though no general theory of fluorine chemical shift exists for covalent framework solids, a general qualitative trend in these oxyfluorinated compounds is that the more fluorine is coordinated to metallic atoms, the more it is shielded. For a bridging fluorine between two aluminums, chemical shifts are in the range -120 ppm, and for a fluorine surrounded by six sodiums in NaF, the chemical shift lies at -220 ppm. This is only one component of the different contributions to fluorine chemical shift, but it provides a good estimate for large differences in chemical shift. A position of about -180 ppm is then consistent with the observed 4-fold coordination of fluorine by vanadiums.

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Supporting Information Available: Table S1, listing of conditions for data collection; Table S2, listing of atomic coordinates; Table S3, listing of anisotropic thermal motions; and Table S4, listing of bond lengths and angles (10 pages). Ordering information is given on any current masthead page.

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(18) Taulelle, F.; Loiseau, T.; Maquet, J.; Livage, J.; Férey, G. *J. Solid State Chem.* **1993**, *105*, 191.

(19) Jameson, C. J. Fluorine. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; Chapter 16.