Hydrothermal synthesis and structural determinations of some new polyoxofluorovanadates $[V_{14}O_{36}F_4]^{8-}$ interleaved by water molecules and organic cations $NH_3(CH_2)_nNH_3$ (n = 4–6)

Cyril Ninclaus, Didier Riou*† and Gérard Férey

Institut Lavoisier, UMR-CNRS C 173, Université de Versailles-St Quentin en Yvelines, 45 Avenue des Etats-Unis, 78035 Versailles Cedex, France

$[V_{14}O_{36}F_4]^{8-}$ **polyanions are built up from two trimers of three edge-sharing VO$_5$F octahedra, two dimers of two square pyramids related by their basal plane, two VO$_4$ tetrahedra and two VO$_4$F trigonal bipyramids; between them are intercalated water molecules and diprotonated amines which stabilize the structures by hydrogen bonds.**

In the course of investigations on microporous materials, we first focused our attention on the hydrothermal behaviour of the quinary systems M$_2$O$_3$ (M = Al, Ga)–P$_2$O$_5$–HF–organic template–H$_2$O. This led to a new series, denoted ULM-n, of fluorinated alumino- and gallo-phosphates of which ULM-5[1] and ULM-16[2] are the more remarkable members. The free apertures of their 16-ring tunnels are 12.2 × 8.3 Å in ULM-5 and 10.4 × 10.4 Å in ULM-16. Recently, we proposed a mechanism for the formation of these phases[3] in which the chemical nature of the metallic element does not play a predominant role. The possibility to substitute completely aluminium or gallium by a 3d transition metal was thus explored and led to the synthesis and characterization of some microporous Fe^{III} compounds with interesting magnetic properties[4–5] and vanadophosphates templated by organic cations.[6,7] We also synthesized the fresnoïte related (NH$_4$)$_2$VO(V$_{2-x}$P$_x$O$_7$) (x *ca.* 1), which shows that V^V and P atoms are statistically distributed on the same tetrahedral sites.[8] If such a substitution is possible in the ULM series containing vanadium, then the existence of vanadium oxides with microporous frameworks could become a reality. The only results reported up to now concern vanadium oxides with lamellar structures V$_2$O$_5$·0.5diamine,[9–11] NMe$_4$V$_4$O$_{10}$[12] and (C$_6$H$_{14}$N$_2$)V$_6$O$_{14}$·H$_2$O.[13]

The title compounds were synthesized hydrothermally using 1,4-diaminobutane (1,4-DAB), 1,5-diaminopentane (1,5-DAP) and 1,6-diaminohexane (1,6-DAH) as organic templates. The aqueous mixture with molar ratio 1 V$_2$O$_5$: 2 HF : 0.8 diamine (1.4 in the case of 1,6-DAH) : 80 H$_2$O was placed in a stainless-steel autoclave lined with Teflon and heated under autogenous pressure at 180 °C for 24 h. The pH of the liquid phase was constant at *ca.* 4–5 during the reaction. The solid phase was filtered off, washed with deionized water and dried in air at room temperature. The prepared products were pure with yields of around 70%. The crystals appear black but are blue after grinding. The crystal morphology of the compound prepared with 1,5-DAP is very striking. A scanning electron micrograph (Fig. 1), performed on a Hitachi S2300, shows that they grow as big hollow needles. Suitable single crystals of both phases intercalating 1,5-DAP and 1,6-DAH were isolated for structural determination‡ by X-ray diffraction. The quality of the crystals prepared with 1,4-DAB was not sufficient to perform the same study. Nevertheless, the IR spectra of the compounds (Fig. 2), recorded on a Nicolet Magna-IR 550 in the range 2000–300 cm^{-1}, show unambiguously that the three polyanions are similar. ν(V=O$_{terminal}$) and ν(V–O$_{bridging}$) are observed at 970 and 750 cm^{-1} respectively, the bands observed around 1500–1600 cm^{-1} are characteristic of –NH$_3^+$. Chemically, we measured for each compound (*i*) the fluorine content by

potentiometric titration with a specific electrode, (*ii*) the vanadium content by redox titration using MnO$_4^-$ and Fe^{2+} for V^{4+} and V^{5+} respectively, (*iii*) the amount of organic template and water by thermogravimetry performed on a SETARAM apparatus operating under air. These measurements give with a very good accuracy the general formula [V$^{4+}_2$V$^{5+}_{12}$O$_{36}$F$_4$]· 4diamine·nH$_2$O (n = 6 for 1,4-DAB, 8 for 1,5-DAP and 4 for 1,6-DAH). In addition, some density measurements were realized on a Micromeritic multipycnometer under He flow for the two compounds whose structures have been solved by single-crystal X-ray diffraction [D_m = 2.01(3) g cm^{-3}, D_c = 2.016 for 1,5-DAP; D_m = 2.01(4), D_c = 1.982 for 1,6-DAH].

V$_{14}$O$_{36}$F$_4$·4N$_2$C$_6$H$_{18}$·4H$_2$O **1** is triclinic and can be described as primitive pseudo-cubic stacking of [V$_{14}$O$_{36}$F$_4$]$^{8-}$ polyanions between which are intercalated the organic cations and the water molecules (Fig. 3). V$_{14}$O$_{36}$F$_4$·4N$_2$C$_5$H$_{16}$·8H$_2$O **2** presents a similar organization but its symmetry is monoclinic and the polyanions are oriented in two different ways. Consequently, two parameters are doubled and $V(\mathbf{2}) = 4\,V(\mathbf{1})$. The decrease of steric hindrance from 1,6-DAH to 1,5-DAP due to the shortening of the aliphatic chain (C$_5$ *vs.* C$_6$) is compensated by the presence of four additional water molecules in **2**.
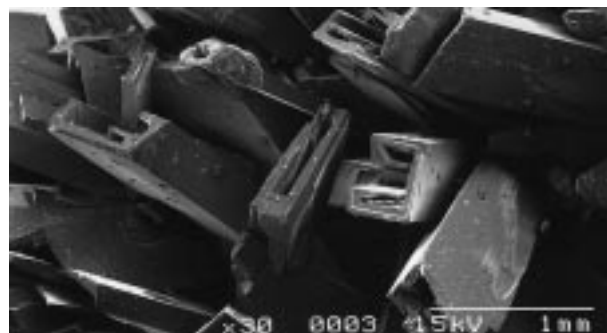

Fig. 1 SE micrograph of V$_{14}$O$_{36}$F$_4$·4N$_2$C$_5$H$_{16}$·8H$_2$O crystals
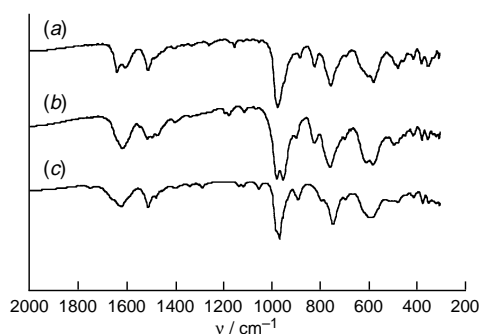

Fig. 2 IR spectra of the polyanionic phases interleaving organic cations NH$_3$(CH$_2$)$_n$NH$_3$ with n = 6 (*a*), 5 (*b*) and 4 (*c*)

The $[V_{14}O_{36}F_4]^{8-}$ anion contains four types of vanadium polyhedra. Two trimers of edge-sharing VO_5F octahedra form the heart of the polyanion. In each trimer, the vertex shared by the three octahedra is fluorine, F^- being characterized by bond valence analysis[14] and thermal parameters in agreement with the previous chemical analysis. Within each trimer, V^{4+} occupies the octahedron which is not linked by edges to one of the four V^VO_5 square pyramids relating the two trimers. The connection exists in such a way that each square pyramid shares an edge with one octahedron of one trimer and the two other O atoms of its basal plane with two octahedra of the opposite trimer (Fig. 4). On the external side of each trimer are grafted a V^VO_4 tetrahedron and a V^VO_4F trigonal bipyramid. Each trigonal bipyramid has three free apices, one of them is occupied by a F atom which gives rise to strong interactions with the H atoms of the amino groups. In **1** and **2**, the polyanions realize the same connectivities between the polyhedra. Nevertheless, in **1** the polyanions are built up around an inversion centre and possess 2×7 independent vanadium atoms whereas in **2**, each polyanion is built up from 14 vanadium atoms resulting from 14 independent crystallographic sites. The attribution of the V^{4+} on one particular site was possible on the basis of the bond valence analysis[14] and on the detailed examination of the distribution of V–O bond lengths in the octahedra (supplementary material available from authors).

The presence of fluorine in a polyanionic phase is generally as encapsulating inside the polyanion where F^- plays the role of
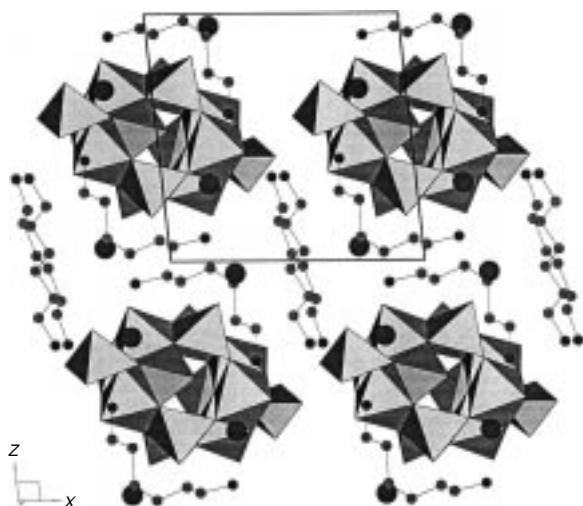
template. Recently, we have shown in the $[V_4(HPO_4)(PO_4)_3O_6F]^{8-}$ polyanions[7] a fluorine atom linked to the vanadium atoms and divided between four VO_5F octahedra building the core of the polyanion. This situation is almost comparable to the octahedral trimers described here and also encountered by Müller et al.[15] in $Na_6[H_6V_{12}O_{30}F_2]\cdot22H_2O$. The originality of **1** and **2** is the presence of a third type of fluorine, located at the outer shell of the polyanion and which stabilizes the whole structure by strong hydrogen bonds.

Footnotes

Fig. 3 Projection along [010] of the structure of $V_{14}O_{36}F_4\cdot4N_2C_6H_{18}\cdot4H_2O$ with a polyhedral model for the $[V_{14}O_{36}F_4]^{8-}$ polyanions and a 'ball and stick' model for the diamines and the water molecules. Large circles refer to water and small circles to 1,6-DAH.
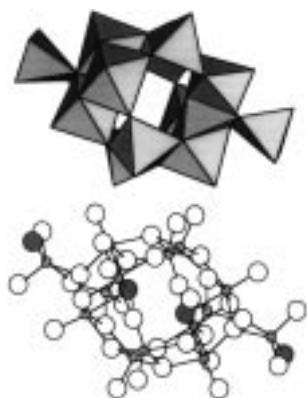

Fig. 4 Polyhedral and 'ball and stick' representations of the $[V_{14}O_{36}F_4]^{8-}$ polyanion. Vanadium atoms are indicated by small circles, oxygen and fluorine atoms with open and large grey circles, respectively.

References

1 Th. Loiseau, D. Riou, F. Taulelle and G. Férey, *Zeolites and Related Microporous Materials: State of the Art 1994, Stud. Surf. Sci. Catal.*, 1994, **84**, 395.
2 Th. Loiseau and G. Férey, *J. Mater. Chem.*, 1996, **6**, 1073.
3 G. Férey, *J. Fluorine Chem.*, 1995, **72**, 187.
4 M. Cavellec, C. Ninclaus, D. Riou, J. M. Grenèche and G. Férey, *Zeolites*, 1996, **17**, 250.
5 M. Cavellec, J. M. Grenèche, D. Riou and G. Férey, *Microporous Mater.*, 1997, **8**, 3.
6 D. Riou and G. Férey, *J. Solid State Chem.*, 1994, **111**, 422.
7 D. Riou, F. Taulelle and G. Férey, *Inorg. Chem.*, 1996, **35**, 6392.
8 C. Ninclaus, R. Retoux, D. Riou and G. Férey, *J. Solid State Chem.*, 1996, **112**, 139.
9 D. Riou and G. Férey, *J. Solid State Chem.*, 1995, **120**, 137.
10 D. Riou and G. Férey, *Inorg. Chem.*, 1995, **34**, 6520.
11 Y. Zhang, R. C. Haushalter and A. Clearfield, *Inorg. Chem.*, 1996, **35**, 4950.
12 P. Y. Zavalij, M. S. Whittingham, E. A. Boylan, V. K. Pecharsky and R. A. Jacobson, *Z. Kristallogr.*, 1996, **211**, 464.
13 L. F. Nazar, B. E. Koene and J. F. Britten, *Chem. Mater.*, 1996, **8**, 327.
14 N. E. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. B*, 1991, **29**, 269.
15 A. Müller, R. Rohlfing, A. L. Barra and D. Gatteschi, *Adv. Mater.*, 1993, **5**, 915.