



An unusual hybrid fluoride featuring a $[V_7F_{27}]^{6-}$ chain motif based on a pyrochlore-like building unit

David W. Aldous, Alexandra M.Z. Slawin, Philip Lightfoot*

EaStChem, School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, UK

ARTICLE INFO

Article history:

Received 26 June 2008

Received in revised form

28 July 2008

Accepted 3 August 2008

Available online 14 August 2008

Keywords:

Vanadium fluoride

Solvothermal synthesis

Chain structure

Pyrochlore

ABSTRACT

A new hybrid vanadium (III) fluoride $[C_4H_{12}N_2]_3[V_7F_{27}]$ has been synthesised solvothermally. The crystal structure (trigonal, $R\bar{3}c$; $a = 17.367(2)\text{Å}$, $c = 19.604(2)\text{Å}$) reveals an unusual and novel chain motif consisting of pyrochlore-like heptameric units of corner-sharing octahedra, which are further linked into linear chains of alternating triple and single octahedral groups. The chains are separated by hydrogen-bonded piperazinium moieties. Magnetic susceptibility data show moderate antiferromagnetic interactions but no long-range order above 2 K, consistent with pronounced one-dimensional character, as well as frustration arising within the triangular units of magnetic ions in the chains.

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1. Introduction

We have recently shown that solvothermal synthesis is a fruitful approach to the preparation of a wide variety of novel hybrid inorganic–organic vanadium fluorides and oxyfluorides (VOFs) [1–4]. In particular, we have shown that the condensation of oligomeric VOF units into chains and layers is dictated by reaction temperature, and the reduction of vanadium oxidation state from +5 to +4 and +3 is influenced by reaction temperature and the inclusion of a co-solvent to water, such as ethylene glycol. These features are nicely illustrated in a focussed study of the V_2O_5 –piperazine–HF– H_2O –ethylene glycol system, using reaction temperature as the only variable, where five distinct phases are produced [4]. Naturally, in such a complex reaction-space, changing one or more of the other variables is likely to produce further new phases; reducing, for example, the organic cation to vanadium ratio is likely to encourage further condensation of the vanadium (oxy)fluoride component in order to balance the smaller cation content with a reduced negative charge on the inorganic sublattice. In this paper we present a simple example of this type of structure-direction and report the isolation of $[C_4H_{12}N_2]_3[V_7F_{27}]$, a piperazinium templated hybrid fluoride which exhibits a unique ‘triple-chain’ vanadium fluoride backbone with a basic building block similar to that in the pyrochlore structure.

2. Experimental

2.1. Synthesis

0.182 g (1.00×10^{-3} mol) of V_2O_5 was weighed into a 30 ml polypropylene bottle and dissolved with 0.5 ml (3.1×10^{-2} mol) of 48% HF at room temperature for 5 min. To this solution 5 ml ethylene glycol was added, followed by 0.086 g (1.00×10^{-3} mol) piperazine. The mixture was heated in a teflon-lined stainless steel autoclave at 190 °C for 24 h, with subsequent cooling to room temperature. Brown prismatic crystals were filtered off and dried at room temperature. Both elemental analysis (Carlo Erba EA1110) and powder X-ray diffraction (Stoe STADI/P powder diffractometer, $CuK\alpha_1$ radiation) confirmed phase purity: calc. (%) for $[C_4H_{12}N_2]_3[V_7F_{27}]$: C 12.71, H 3.20, N 7.41; found: C 12.91, H 3.10, N 7.10.

2.2. X-ray crystallography

Single crystals were analysed using a Rigaku Mercury CCD equipped with graphite monochromated $MoK\alpha$ radiation. Intensity data were collected by the narrow frame method at 93 K and corrected for Lorentz and polarisation effects as well as absorption by Multi-Scan techniques. The structure was solved by direct methods and refined by full-matrix least-squares cycles in SHELX-97. All non-H atoms were refined with anisotropic thermal parameters. H atoms were refined as riding atoms. There is two-fold disorder of the N atoms of the piperazinium moiety; this may be in part responsible for the relatively high *R*-factors, although all

* Corresponding author. Fax: +44 1334 463808.

E-mail address: pl@st-and.ac.uk (P. Lightfoot).

Table 1
Crystallographic data for $[\text{C}_4\text{H}_{12}\text{N}_2]_3[\text{V}_7\text{F}_{27}]$

Space group	$R\bar{3}c$
a (Å)	17.367(2)
c (Å)	19.604(2)
V (Å ³)	5120.6(9)
Z	6
ρ_{calc} (g cm ⁻³)	2.207
μ (mm ⁻¹)	2.000
Crystal size (mm)	0.17 × 0.15 × 0.10
$F(000)$	3324
Reflns collected	16,123
Independent reflns	1316
R_{int}	0.078
Obsd data [$I > 2\sigma(I)$]	977
Data/restraints/parameters	1316/0/89
GOF on F^2	1.295
$R1, wR2$ [$I > 2\sigma(I)$]	0.1257, 0.1819
$R1, wR2$ (all data)	0.1709, 0.1987

Table 2
Selected bond lengths (Å) and bond valences, s_{ij} (valence units) for $[\text{C}_4\text{H}_{12}\text{N}_2]_3[\text{V}_7\text{F}_{27}]$

Bond	Bond length (Å)	s_{ij}
V1–F1	1.980(2)	0.47
V1–F2	2.006(5)	0.44
V1–F2'	1.965(5)	0.49
V1–F3	1.871(5)	0.64
V1–F4	1.828(5)	0.71
V1–F5	1.994(5)	0.45
	$\sum V1 = 3.20$	
	$\sum F1 = 0.94$	
	$\sum F2 = 0.91$	
	$\sum F3 = 0.64$	
	$\sum F4 = 0.71$	
	$\sum F5 = 0.52$	
V2–F5 × 6	1.939(5)	0.52
	$\sum V2 = 3.12$	
	$\sum F5 = 0.97$	

atoms are well-behaved. Crystallographic data are provided in Tables 1 and 2 and in the Supplementary file (CIF format): CCDC deposition number 696687 (this will be added at Proof stage—PL).

3. Magnetic measurements

Magnetic data were measured on a Quantum Design MPMS SQUID. Data were recorded in 5000 Oe field while warming the sample from 2 K to 334 K in 4 K steps, following consecutive zero field cooling (ZFC) and field cooling (FC) cycles.

4. Results and discussion

The crystal structure of $[\text{C}_4\text{H}_{12}\text{N}_2]_3[\text{V}_7\text{F}_{27}]$ features a basic inorganic building unit (Fig. 1) which consists of two distinct octahedral vanadium sites (both confirmed as V^{3+} by bond valence sum analysis [5], Table 2). V(1) is situated on a general position, whereas V(2) occupies a high symmetry ($\bar{3}$) position and shares F(5) corners with six neighbouring V(1) sites to form the heptameric unit shown in Fig. 2. The V(2) octahedra are, in turn, linked to neighbouring V(2) octahedra within the same heptamer via F(2) bridges, and to neighbouring heptamers via F(1) bridges. The result of this is that neighbouring heptameric units are further linked into an infinite chain along the c -axis via the bridging F(1) sites, such that V(1) has four bridging F ligands (F(1), F(2) F(2)' and F(5)) and two terminal ones (F(3) and F(4)). There

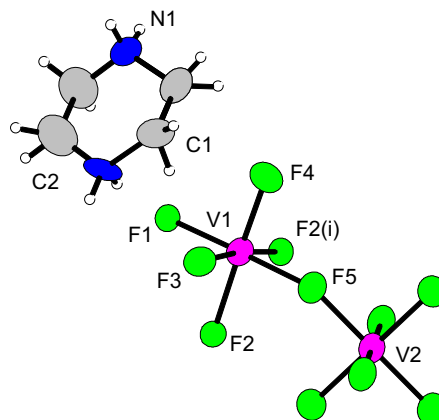


Fig. 1. Basic building unit. Note only one conformation of the two-fold disordered piperazinium moiety is shown. Atoms drawn as 50% probability ellipsoids. Symmetry operator (i) $-y, x-y, z$.

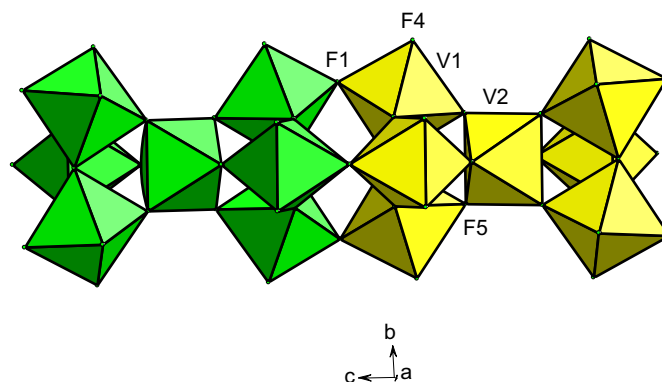


Fig. 2. The $[\text{V}_7\text{F}_{27}]_n$ chain structure, with pyrochlore-like heptameric unit highlighted. Note that two linked heptameric building blocks constitute the unit cell repeat along the c -axis.

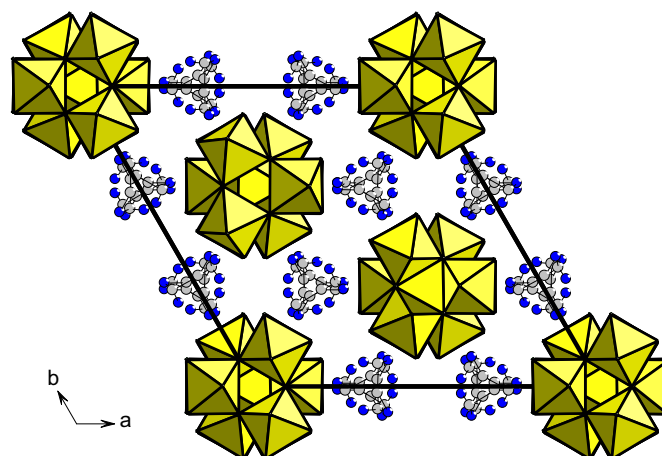


Fig. 3. Projection of the structure down the c -axis showing the $[\text{V}_7\text{F}_{27}]_n$ chains separated by the piperazinium moieties.

are two linked heptameric units per repeat unit cell along the c -axis (Fig. 2).

The inorganic chains are separated by the piperazinium moieties, which form significant hydrogen bond contacts with the terminal fluorine atoms $\text{N}(1a)\text{—F}(3)$ 2.59 Å, $\text{N}(1)\text{—F}(4)$ 2.57 Å (Fig. 3); these interactions are also manifested in the reduced bond valence sums at these F sites; Table 2). The resulting 'sausage-like'

$[V_7F_{27}]^{6-}$ chain (Fig. 2) which exhibits alternating trimeric and monomeric ‘links’ in a 3-3-1 configuration, is unique in metal fluoride chemistry. The majority of chain-structure fluorides [6] correspond to the stoichiometry A_xMF_5 , and are characterised by octahedral $[MF_4F_{2/2}]$ units sharing either *trans*- or *cis*-vertices. Mechanisms which allow the formation of fluoride chains with reduced F/M ration include face-shared single chains (such as in the hexagonal perovskite $CsNiF_3$), ‘double’ octahedral chains in Ba_2CoFeF_9 and, most pertinently in the present context, structure types based on either the heptameric building unit itself or on ‘triple’ corner-sharing octahedral chains.

The heptameric building unit may be considered as the basic building block of the pyrochlore structure, in which case it is connected via all external corners into a three-dimensional array. It has been observed previously as an isolated anionic unit in the hybrid aluminium fluoride $[H_4tren]_2(H_3O) \cdot [Al_7F_{30}]$ [7] (*tren* = tris(2-aminoethyl)amine) and also as a building block in two chain-structure aluminium fluorides: $[H_4tren]_2[Al_7F_{29}] \cdot 2H_2O$ [7] and $[H_4tren]_{3/2}[Al_6F_{24}] \cdot 3H_2O$ [8]. In the former case these units are linked through terminal F atoms, whereas in the latter they are fused via a common AlF_6 octahedron. These two chains, along with the triple chain in $KCrF_4$ [9] and $CsCrF_4$ [10] are shown in Fig. 4. The two latter compounds have been studied for potentially interesting magnetic properties [11,12], as they are based on an intrinsically frustrated triangular motif [13,14]. More recently, in the light of the resurgence of interest in magneto-electric or multiferroic materials, $KCrF_4$ has been analysed for potential magnetoelectric properties [15]. Within vanadium-

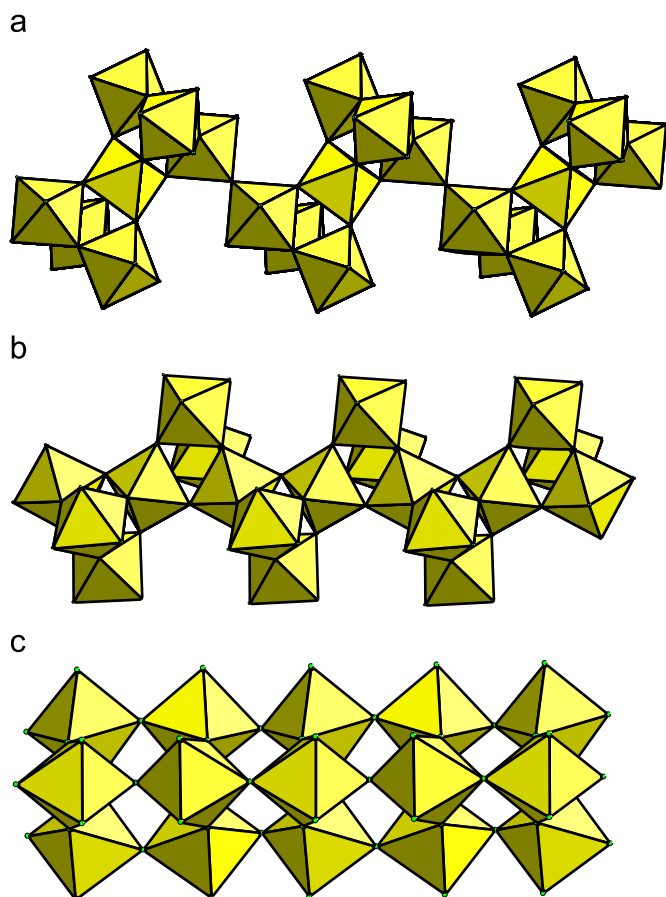


Fig. 4. (a) Linkage of heptameric $[M_7F_{30}]$ units into chains in $[H_4tren]_2[Al_7F_{29}] \cdot 2H_2O$. (b) Linkage of heptameric $[M_7F_{30}]$ units into chains in $[H_4tren]_{3/2}[Al_6F_{24}] \cdot 3H_2O$. (c) Linkage of trimeric $[M_3F_{15}]$ units into chains in $KCrF_4$ and $CsCrF_4$.

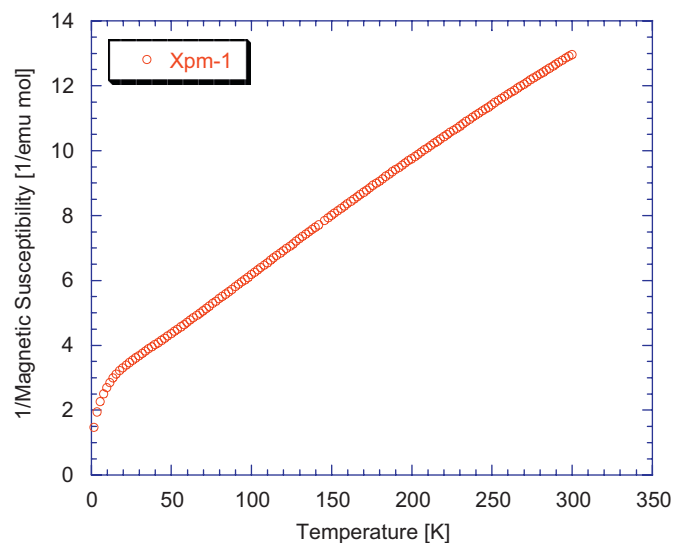


Fig. 5. $1/\chi$ vs. T plot for $[C_4H_{12}N_2]_3[V_7F_{27}]$.

containing compounds there are also examples of ‘triangular’ frustration, for example in the three-dimensionally connected pyrochlore $pyr-VF_3$ [16] and a V^{III} carboxylate containing isolated trimeric vanadium moieties [17].

The magnetic susceptibility data for $[C_4H_{12}N_2]_3[V_7F_{27}]$ are presented in Fig. 5. The plot of $1/\chi$ vs. T shows paramagnetic behaviour down to 20 K and a Curie–Weiss fit yields parameters $\mu_{eff} = 2.92(2)$ BM (which is close to the theoretical value of 2.82 BM per V^{3+}) and $\theta = -77.5$ K, suggesting reasonably strong antiferromagnetic interactions. The near-neighbour V–V distances within each chain are $V1-V2 = 3.71$ Å, $V1-V1 = 3.78$ Å, whereas the nearest *inter-chain* distances are around 6.7 Å, therefore there are unlikely to be significant *inter-chain* magnetic interactions. The fact that there is no long-range magnetic ordering observed above 2 K may suggest that there may indeed be magnetic frustration present, however the lack of ordering in one-dimensional systems is also well-known to be caused by entropy effects, and the lack of any deviation between field-cooled and zero field-cooled magnetic data reveal no conclusive evidence for frustration in this case.

The discovery of the title compound arose from our more detailed survey of the solvothermal chemistry of the V_2O_5 –piperazine–HF– H_2O –ethylene glycol system. Reaction of 1 mmol of V_2O_5 with 0.5 ml 48% HF, 5 ml ethylene glycol, 3 ml H_2O and 3 mmol piperazine at 190 °C for 24 h produced the *cis*-octahedral chain-structure $[C_4H_{12}N_2][VF_5] \cdot H_2O$ [3,4]. $[C_4H_{12}N_2]_3[V_7F_{27}]$ is obtained by an analogous reaction, but by reducing the piperazine content by a factor of 3 and also omitting the water as solvent. The consequent reduction in the template: vanadium ratio of the product naturally gives rise to a lower F/V ratio, since a lower net negative charge per V atom is required, and ultimately a more ‘condensed’ inorganic structural component. It is likely that similar strategies will extend the structural chemistry of vanadium fluorides still further.

Appendix A. Supplementary material

CCDC 696687 contains the supplementary crystallographic data. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

We thank Prof. Andrew Harrison for helpful discussions and the University of St. Andrews and EPSRC for funding.

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