metal-organic compounds

A new chain structure: *catena*-poly-[4,4′-(ethane-1,2-diyl)dipyridinium bis[[aquadifluoridooxidovanadate]-*μ*-fluorido]]

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

School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: pl@st-and.ac.uk

The title compound, $\{(C_{12}H_{12}N_2)[V_2F_6O_2(H_2O)_2]\}_n$, features a novel extended-chain moiety, $[VOF_2F_{2/2}(H_2O)]_n$, comprising *trans* vertex-connected $VOF_4(H_2O)$ octahedra. The octahedra themselves show the characteristic distortion due to the off-centring of the V^{4+} ion, such that a short terminal V=O bond and an elongated *trans* V—OH$_2$ bond are present. Hydrogen bonding from the water molecules to terminal F atoms in adjacent chains generates associated chain dimers, which are loosely linked into sheets *via* additional hydrogen bonding involving the organic moieties. Structural relationships with previously described vanadium oxyfluoride species are briefly discussed.

Comment

The title compound, (I), was isolated during a more general survey of the solvothermal chemistry of vanadium oxy-fluorides incorporating organic amines (Aldous *et al.*, 2007a,b).
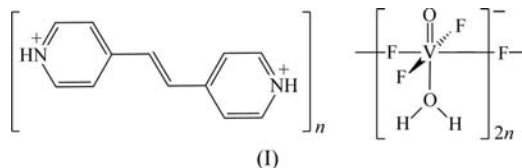
The building unit of (I) (Fig. 1) exhibits a single V site in a distorted octahedral environment and a diprotonated 4,4′-(ethane-1,2-diyl)dipyridinium ligand (bpeH$_2$) located on an inversion centre. The short V=O and longer *trans* V—OH$_2$ bond lengths are comparable with those seen in previous examples of the polar $VOF_4(H_2O)$ moiety (Stephens *et al.*, 2005; Aldous *et al.*, 2007a). The octahedral units are linked through *trans* fluoride ligands, F1, to produce a novel infinite chain motif.
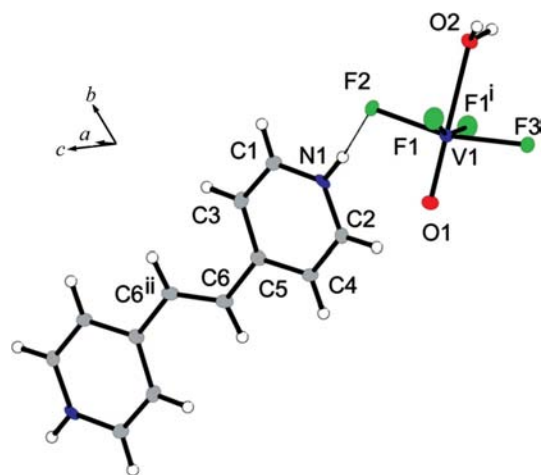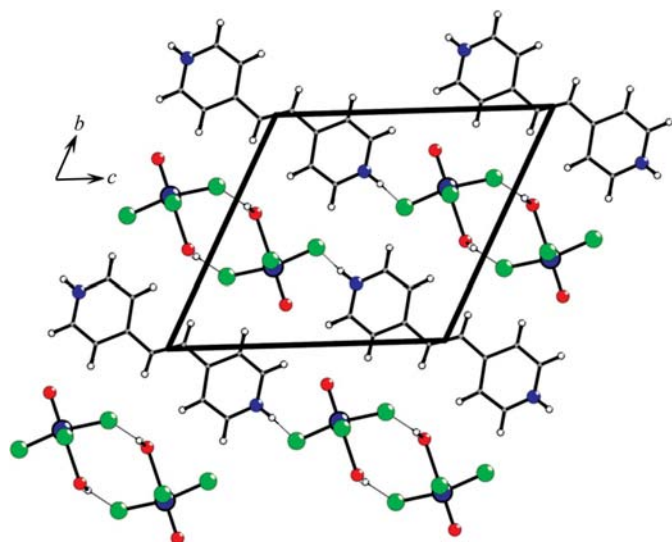

Figure 1
The building unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-1 + x, y, z$; (ii) $-2 - x, -y, 2 - z$.]
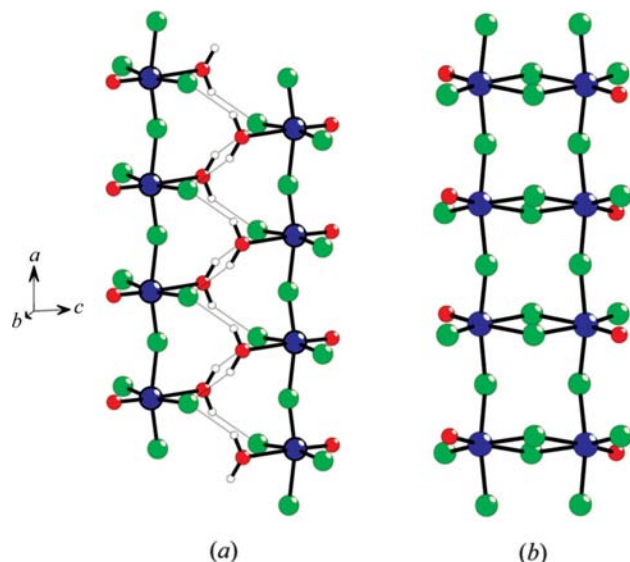
Figure 2
(*a*) Pairs of hydrogen-bonded (fine lines) anionic chains of (I), extending along [100]. (*b*) Ladder-like chains of stoichiometry (VOF$_3$), observed previously in (bpeH$_2$)[VOF$_3$]$_2$ (Aldous, Goff *et al.*, 2007). By comparison with (*a*), the condensation of the hydrogen-bonded chains in (I) to ladders in this compound can be visualized.

Bond-valence sum analysis (Brese & O'Keeffe, 1991) (Table 1) confirms the assignment of the V centre as V^{4+}, and reveals underbonding at the terminal F sites F2 and F3. These sites therefore accept hydrogen bonds, F3 from the water molecules in neighbouring chains and F2 from the organic group (Table 2). This results in pairs of associated inorganic chains (Fig. 2a), which are weakly associated into layers *via* the bpeH$_2$ ligands (Fig. 3).

Apart from the novelty of the chain unit itself, the most significant feature of this structure lies in the relationship of the chain architecture to the 'ladder-like' (VOF$_3$) chains previously observed in the same synthetic system. The ladder units in $(C_{12}H_{12}N_2)[VOF_3]_2$ (Aldous, Goff *et al.*, 2007) are

Figure 3
The crystal packing of (I), viewed along [100], showing the chain dimers and further hydrogen bonding (fine lines) from the bpeH$_2$ moieties.

shown in Fig. 2(*b*). This compound was prepared from an identical reaction mixture under identical reaction conditions to those used for (I), except that the temperature was raised from 333 to 373 K for the ladder. One can therefore speculate that, in the preparation of the ladder phase, hydrogen-bonded dimerized chains of the type observed in (I) (Fig. 2*a*) are formed initially and then condense into the ladder chains at elevated temperatures *via* the loss of the water ligands and fusion of adjacent chains through bonding of terminal F atoms, F3 in the case of (I), to the adjacent V centre. We have also shown recently (Himeur *et al.*, 2010) that a similar condensation mechanism could occur to produce extended sheet architectures of composition VOF$_{2.5}$ from VOF$_3$ ladders by using a different solvent, in fact, an ionic liquid. The isolation of (I) therefore adds a 'missing piece of the jigsaw' in understanding the formation of extended vanadium oxyfluorides from oligomeric building blocks in solvothermal systems.

We also note that further examples of a 'VOF$_3$(H$_2$O)' compositional group occur in the Cambridge Structural Database (CSD, Version 5.31; Allen, 2002), but these apparent compositional similarities to (I) belie any exact structural similarity, as the previous examples are based upon edge-sharing dimeric units, 'V$_2$O$_2$F$_6$(H$_2$O)$_2$', with either axial (Bukovec *et al.*, 1981; Demsar & Bukovec, 1984) or equatorial (Aldous *et al.*, 2007*b*) H$_2$O groups, rather than the present infinite chain motif.

Experimental

Vanadium pentoxide (0.1819 g), water (5 ml) and a 40% solution of HF (0.5 ml) were heated in a polypropylene bottle at 373 K for 1 h. To the contents of the bottle, ethylene glycol (5 ml) and 4,4′-(ethane-1,2-diyl)dipyridine (0.5338 g) were added. The resulting mixture was heated at 333 K for 2 d and then allowed to cool naturally to ambient temperature. The final product was filtered off, washed with water and allowed to dry overnight at 333 K. Crystals of (I) are blue platelets of typical dimensions 0.2 × 0.1 × 0.01 mm. Phase purity was

Table 1
Bond-valence parameters.

s_{ij} values are calculated for $B = 0.37$.

Atom	Σs_{ij}	Reference
V1	4.15	
O1	1.62	*a*
O2	0.28	*a*
F1	0.69	*b*
F1	0.46	*b*
F2	0.56	*b*
F3	0.54	*b*

References: (*a*) Brown & Altermatt (1985), empirical; (*b*) Brese & O'Keeffe (1991), extrapolated.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$F2	0.88	1.75	2.622 (3)	170
O2—H11$\cdots$F3^i	0.83 (2)	1.82 (2)	2.640 (3)	167 (4)
O2—H12$\cdots$F3^{ii}	0.83 (2)	1.88 (2)	2.682 (3)	162 (4)

Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $-x + 1, -y + 1, -z$.

confirmed by powder X-ray diffraction of the bulk product and by elemental analysis; found (%): C 31.32, H 3.20, N 5.93; calculated for C$_{12}$H$_{16}$F$_6$N$_2$O$_4$V$_2$ (%): C 30.79, H 3.44, N 5.98. Magnetic susceptibility measurememments revealed (I) to be paramagnetic down to 2 K.

Crystal data

(C$_{12}$H$_{12}$N$_2$)[V$_2$F$_6$O$_2$(H$_2$O)$_2$]	$\gamma = 87.60$ (4)°
$M_r = 468.15$	$V = 390.3$ (2) Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 3.7797$ (17) Å	Mo $K\alpha$ radiation
$b = 10.362$ (3) Å	$\mu = 1.29$ mm^{-1}
$c = 11.297$ (3) Å	$T = 93$ K
$\alpha = 62.92$ (2)°	0.12 × 0.10 × 0.02 mm
$\beta = 82.30$ (3)°	

Data collection

Rigaku Mercury CCD area-detector diffractometer	2526 measured reflections
	1385 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)	1215 reflections with $I > 2\sigma(I)$
$T_{min} = 0.864$, $T_{max} = 1.000$	$R_{int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.080$	
$S = 1.08$	
1385 reflections	$\Delta\rho_{max} = 0.36$ e Å^{-3}
126 parameters	$\Delta\rho_{min} = -0.34$ e Å^{-3}
2 restraints	

H atoms attached to C and N atoms were placed in geometrically idealized positions and refined using a riding model, with C—H = 0.95 Å and N—H = 0.88 Å, and with U_{iso}(H) = $1.2U_{eq}$(C,N). Water H atoms were located in a difference Fourier map and then refined isotropically with an O—H bond-length restraint of 0.85 (2) Å.

Data collection: *CrystalClear-SM* (Rigaku, 2009); cell refinement: *CrystalClear-SM*; data reduction: *CrystalClear-SM*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics:

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DIAMOND (Brandenburg, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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