

Crstal structure of tri-guanidinium hexafluorovanadate(III), $[\text{CN}_3\text{H}_6]_3[\text{VF}_6]$; an unusual hybrid perovskite-related compound

Cameron Black and Philip Lightfoot*

School of Chemistry, EaStCHEM, University of St Andrews, KY16 9ST

Correspondence email: pl@st-andrews.ac.uk

Abstract

The title compound has a cubic structure, space group $Pa\bar{3}$, exhibiting isolated regular VF_6 octahedral units, which are hydrogen-bonded to protonated guanidinium moieties. Although the VF_6 octahedral units are not linked directly together, there are structural similarities between this crystal structure and those of the wider family of perovskite materials, in particular hybrid perovskites based on extended ligands such as cyanide. In this context the octahedral tilt system of the present compound is of interest, and demonstrates that unusual tilt systems can be mediated *via* 'molecular' linkers which allow only supramolecular rather than covalent interactions.

1. Introduction

Solvothermal synthetic routes to vanadium fluorides have proved fruitful in preparing new compounds with novel crystal-chemical features and interesting physical properties. In some of our recent work we have prepared vanadium fluorides and oxyfluorides exhibiting vanadium in oxidation state +3, +4 and +5 and also mixed valence systems, with vanadium typically in octahedral coordination. The VF_6 or VOF_5 octahedral units may be linked into structures of varying dimensionality, for example oligomeric units, chains or layer structures (Aldous *et al.*, 2007; Aidoudi *et al.*, 2014a; Aidoudi *et al.*, 2014b). Here we present a novel vanadium(III) fluoride, $[\text{CN}_3\text{H}_6]_3[\text{VF}_6]$, containing discrete VF_6 octahedral units, linked *via* hydrogen-bonded guanidinium moieties into a cubic supramolecular array which has similarities to the perovskite structural family.

2. Experimental

The title compound was prepared solvothermally: V_2O_5 (1 mmol, 0.182 g) and guanidinium carbonate (0.5 mmol, 0.091 g) were dissolved in 0.5 ml 48% HF (aq.). A 5:3 ratio of water (2.5 mL) and ethylene glycol (1.5 ml) was added. The mixture was heated in a sealed Teflon-lined stainless steel autoclave at 160 °C for 72 hrs. The product was clearly inhomogenous, both to the naked eye and according to powder X-ray diffraction, but green crystals of the minor product could be isolated and analysed.

Crystal data, data collection and structure refinement details are summarized in Table 1. All hydrogen atoms were located in Fourier maps and refined isotropically.

3. Results and discussion

$[\text{CN}_3\text{H}_6]_3[\text{VF}_6]$ crystallizes in the cubic space group $Pa\bar{3}$. There are two vanadium sites in the asymmetric unit; although crystallographically distinct, there are no chemically significant differences, both adopting a regular octahedral environment with six equivalent F ligands ($\text{V1} - \text{F1} = 1.946$ (7) Å, $\text{V2} - \text{F2} = 1.945$ (6) Å). Bond valence analysis (Bresle and O'Keeffe, 1991) supports the assertion that vanadium is trivalent (bond valence sums of 3.10 and 3.11 for V1 and V2, respectively). The vanadium octahedra lie at the corners, edge-centres and face-centres of the cubic unit cell, thus defining eight "mini-cube" sub-cells. Protonated guanidinium cations $(\text{CN}_3\text{H}_6)^+$ are located at the approximate face-centres of each of these minicubes (Figure 1) and are positionally ordered, such that they display an "up-down"

alternation along each principal crystallographic axis. All six N—H bonds act as H-bond donors to neighbouring fluoride ions (Figure 2, Table 2).

The resulting structure is reminiscent of the well known perovskite family, ABX_3 , which consists of an infinite cubic array of corner-linked BX_6 octahedra encapsulating a large cation, A, at the "body-centre" position of the resulting cube. In this case, however, there are no direct covalent linkages between neighbouring octahedra, but there are cooperative interactions mediated by the H-bonded guanidinium moieties. Another significant difference is that the guanidinium resides on each of the *faces* of the minicubes, not at the centres, hence leading to the 3:1 A:B (" A_3BX_6 ") rather than 1:1 stoichiometry, and also leaving a large void space at the cube-centre in the present case. We note that a 3:1 stoichiometry, A_3BX_6 , already exists in perovskite crystallography, in the cation-ordered cryolite-type structure: for example, Na_3VF_6 adopts this structure type, where Na fills 50% of the B-sites, in an ordered arrangement, in addition to all of the A-sites (Alter and Hoppe, 1975). The present structure type is very different, despite the similar stoichiometry.

A key characteristic of perovskite crystallography is the cooperative "tilting" of octahedral BX_6 units (Glazer, 1972; Woodward, 1997). The rigid connectivity in conventional perovskites means that tilting of one octahedron dictates tilting, in the opposite sense, of all directly linked octahedra within a plane perpendicular to the tilt axis. However, new families of "hybrid" perovskites have recently been described, which are based on extended polyatomic (rather than monatomic) bridging ligands, such as azide, cyanide or dicyanometallate (Du *et al.*, 2014; Duycker *et al.*, 2016; Hill *et al.*, 2016). This provides enhanced flexibility of the BX_6 framework, and allows tilt patterns that are "forbidden" in conventional perovskites. For example, the compounds $[PPN]Cd[Ag(CN)_2]_3 \cdot 3EtOH$ and $(NMe_4)_2[FeK(N_3)_6]$ both display a pattern of tilts in which "columns" of adjacent, linked octahedra tilt "in-phase", in a direction perpendicular to the tilt axis (Figure 3). As can be seen from Figure 1, the title compound exhibits exactly the same tilt pattern as these previously reported, fully connected perovskites, but in this case the cooperative tilting is mediated *via* the H-bonded countercations, not directly by covalent linkers. In each of these three compounds, the resultant space group is $Pa\bar{3}$. In the case of $(NMe_4)_2[FeK(N_3)_6]$, the crystal transforms to a higher symmetry parent, $Fm\bar{3}m$, at higher temperature, due to disordering of both the tilts and the A-site cation; the unit cell size is retained, however, due to the ordered cation arrangement at the B-sites. In the present case, the parent phase could be envisioned to have a unit cell with $a_p = a/2$, and a space group $Pm\bar{3}m$, if the tilting is lost and the guanidinium cations are allowed to disorder. Hence, the "doubled" unit-cell parameter of the observed structure is caused by the simultaneous, and apparently cooperative, ordering of the guanidinium cations and the octahedral tilting pattern.

Hill *et al.* (2016) have recognized the potential for more complex "forbidden" tilts in hybrid perovskites, and have formulated a means of describing these systems, which necessarily goes beyond the well established Glazer system (Glazer, 1972). It is likely that such a system could be adapted further to incorporate examples such as the present one, whereby the additional degrees of freedom provided through using only non-covalent cooperativity between octahedral units is introduced.

Table 1

Experimental details

Crystal data	
Chemical formula	$F_6V \cdot 3(CH_6N_3)$
M_r	345.20
Crystal system, space group	Cubic, $Pa\bar{3}$
Temperature (K)	173
a (Å)	14.095 (3)

V (\AA^3)	2800.2 (18)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.78
Crystal size (mm)	$0.08 \times 0.07 \times 0.05$

Data collection	
Diffractometer	Rigaku SCXmini
Absorption correction	Multi-scan
T_{\min} , T_{\max}	0.727, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16185, 853, 778
R_{int}	0.093
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.161, 1.32
No. of reflections	853
No. of parameters	83
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e \AA^{-3})	0.44, -0.70

Computer programs: *CrystalClear-SM Expert 2.1 b32* (Rigaku, 2014), *SHELXL2014/7* (Sheldrick, 2008), *Diamond* (Brandenburg, 2009), *WinGX* (Farrugia, 2012).

Acknowledgements

We thank EPSRC for a DTA studentship (EP/P505097/1) to CB.

References

- Aidoudi, F. H., Black, C., Arachchige, K. S. A., Slawin, A. M. Z., Morris, R. E. & Lightfoot, P. (2014a). *Dalton Trans.*, **43**, 568-575.
- Aidoudi, F. H., Downie, L. J., Morris, R. E., de Vries, M. A. & Lightfoot, P. (2014b). *Dalton Trans.*, **43**, 6304-6307.
- Aldous, D. W., Stephens, N. F. & Lightfoot, P. (2007). *Inorg. Chem.* **46**, 3996-4001.
- Alter, E. & Hoppe, R. (1975). *Z. Anorg. Allg. Chem.*, **412**, 110-120.
- Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* **B47**, 192-197.
- Du, Z.-Y., Zhao, Y.-P., He, C.-T., Wang, B.-Y., Xue, W., Zhou, H.-L., Bai, J., Huang, B., Zhang, W.-X. & Chen, X.-M. (2014). *Cryst. Growth Des.* **14**, 3903-3909.
- Duycker, S. G., Hill, J. A., Howard, C. J. & Goodwin, A. G. (2016). *J. Amer. Chem. Soc.*, **138**, 11121-11123.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849-854.
- Glazer, A. M. (1972). *Acta Cryst.* **B28**, 3384-3392.
- Hill, J. A., Thompson, A. L. & Goodwin, A. L. (2016). *J. Amer. Chem. Soc.*, **138**, 5886-5896.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112-122.
- Woodward, P. M. (1997). *Acta Cryst.* **B53**, 32-43.

Figure 1

Fig. 1. Crystal packing viewed along the [100] direction. $[\text{VF}_6]$ moieties are shown as filled octahedra.

Figure 2

Fig. 2. Hydrogen-bonding of the guanidinium moieties to the VF_6 octahedra. $^i = y, z, x$, $^{ii} = -y, 1/2 + z, 1/2 - x$

Figure 3

Fig. 3. Crystal packing of $(\text{NMe}_4)_2[\text{FeK}(\text{N}_3)_6]$. Arrows show the relative direction of rotation of linked octahedra. Note that within each 'column' of octahedra along the a -axis the octahedra rotate in the same sense: this is impossible in conventional perovskites.

supporting information

Crstal structure of tri-guanidinium hexafluorovanadate(III), [CN₃H₆]₃[VF₆]; an unusual hybrid perovskite-related compound

Computing details

Data collection: *CrystalClear*-SM Expert 2.1 b32 (Rigaku, 2014); cell refinement: *CrystalClear*-SM Expert 2.1 b32 (Rigaku, 2014); data reduction: *CrystalClear*-SM Expert 2.1 b32 (Rigaku, 2014); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2008); molecular graphics: *Diamond* (Brandenburg, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

(I)

Crystal data

F₆V·3(CH₆N₃)
M_r = 345.20
 Cubic, *Pa*3̄
a = 14.095 (3) Å
V = 2800.2 (18) Å³
Z = 8
F(000) = 1408
D_x = 1.638 Mg m⁻³

Mo *K*α radiation, λ = 0.71075 Å
 Cell parameters from 800 reflections
 θ = 2.5–25.3°
 μ = 0.78 mm⁻¹
T = 173 K
 Block, green
 0.08 × 0.07 × 0.05 mm

Data collection

Rigaku SCXmini
 diffractometer
 Detector resolution: 14.7059 pixels mm⁻¹
 profile data from φ-scans
 Absorption correction: multi-scan
T_{min} = 0.727, *T_{max}* = 1.000
 16185 measured reflections

853 independent reflections
 778 reflections with *I* > 2σ(*I*)
R_{int} = 0.093
 θ_{max} = 25.3°, θ_{min} = 2.5°
h = -16→16
k = -16→14
l = -16→16

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2σ(*F*²)] = 0.046
wR(*F*²) = 0.161
S = 1.32
 853 reflections
 83 parameters
 0 restraints

Hydrogen site location: difference Fourier map
 All H-atom parameters refined
w = 1/[σ²(*F_o*²) + (0.089*P*)² + 0.3869*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.44 e Å⁻³
 Δρ_{min} = -0.70 e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
V1	0.0000	0.0000	0.0000	0.0124 (5)
V2	0.0000	0.0000	0.5000	0.0125 (5)
F1	-0.02491 (10)	0.02779 (10)	0.13294 (10)	0.0191 (5)
F2	0.02648 (11)	0.02032 (10)	0.36612 (10)	0.0193 (5)
N1	0.02433 (19)	0.35925 (18)	0.25208 (15)	0.0254 (7)
N2	0.01649 (17)	0.22012 (18)	0.16926 (18)	0.0243 (6)
N3	0.04043 (18)	0.21871 (18)	0.33114 (17)	0.0248 (6)
C1	0.0273 (3)	0.2656 (2)	0.25114 (15)	0.0187 (7)
H1	0.0158 (19)	0.389 (2)	0.201 (2)	0.023 (7)*
H2	0.0294 (18)	0.391 (2)	0.304 (2)	0.023 (7)*
H3	0.008 (2)	0.255 (2)	0.117 (3)	0.030 (10)*
H4	0.013 (2)	0.165 (3)	0.171 (2)	0.023 (8)*
H5	0.038 (3)	0.248 (2)	0.383 (3)	0.040 (10)*
H6	0.0386 (19)	0.164 (2)	0.333 (2)	0.017 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V1	0.0124 (5)	0.0124 (5)	0.0124 (5)	0.0002 (2)	0.0002 (2)	0.0002 (2)
V2	0.0125 (5)	0.0125 (5)	0.0125 (5)	-0.0002 (2)	-0.0002 (2)	0.0002 (2)
F1	0.0222 (8)	0.0191 (8)	0.0159 (8)	0.0005 (7)	0.0016 (6)	-0.0009 (6)
F2	0.0223 (9)	0.0200 (8)	0.0157 (8)	-0.0014 (7)	0.0015 (6)	0.0007 (6)
N1	0.0413 (15)	0.0169 (14)	0.0179 (15)	-0.0017 (10)	-0.0005 (10)	-0.0010 (9)
N2	0.0387 (14)	0.0144 (12)	0.0199 (13)	-0.0015 (10)	0.0010 (10)	0.0001 (10)
N3	0.0390 (15)	0.0175 (13)	0.0179 (12)	0.0013 (10)	0.0001 (10)	0.0004 (10)
C1	0.0184 (14)	0.0199 (14)	0.0177 (15)	-0.0022 (12)	0.0020 (9)	-0.0011 (9)

Geometric parameters (\AA , $^\circ$)

V1—F1 ⁱ	1.9461 (15)	V2—F2	1.9448 (15)
V1—F1 ⁱⁱ	1.9461 (15)	N1—C1	1.321 (4)
V1—F1 ⁱⁱⁱ	1.9461 (15)	N1—H1	0.85 (3)
V1—F1 ^{iv}	1.9461 (15)	N1—H2	0.86 (3)
V1—F1 ^v	1.9461 (15)	N2—C1	1.329 (4)
V1—F1	1.9462 (15)	N2—H3	0.89 (4)
V2—F2 ^{vi}	1.9448 (15)	N2—H4	0.78 (3)
V2—F2 ^{vii}	1.9448 (15)	N3—C1	1.320 (3)
V2—F2 ^{viii}	1.9448 (15)	N3—H5	0.84 (4)
V2—F2 ^{ix}	1.9448 (15)	N3—H6	0.77 (3)
V2—F2 ^x	1.9448 (15)		
F1 ⁱ —V1—F1 ⁱⁱ	180.00 (13)	F2 ^{vi} —V2—F2 ^x	180.0
F1 ⁱ —V1—F1 ⁱⁱⁱ	90.93 (6)	F2 ^{vii} —V2—F2 ^x	89.14 (6)
F1 ⁱⁱ —V1—F1 ⁱⁱⁱ	89.07 (6)	F2 ^{viii} —V2—F2 ^x	90.86 (6)
F1 ⁱ —V1—F1 ^{iv}	89.07 (6)	F2 ^{ix} —V2—F2 ^x	89.14 (6)
F1 ⁱⁱ —V1—F1 ^{iv}	90.93 (6)	F2 ^{vi} —V2—F2	89.14 (6)
F1 ⁱⁱⁱ —V1—F1 ^{iv}	89.07 (6)	F2 ^{vii} —V2—F2	90.86 (6)
F1 ⁱ —V1—F1 ^v	90.93 (6)	F2 ^{viii} —V2—F2	89.14 (6)
F1 ⁱⁱ —V1—F1 ^v	89.07 (6)	F2 ^{ix} —V2—F2	180.0

F1 ⁱⁱⁱ —V1—F1 ^v	90.93 (6)	F2 ^x —V2—F2	90.86 (6)
F1 ^{iv} —V1—F1 ^v	180.00 (9)	C1—N1—H1	120 (2)
F1 ⁱ —V1—F1	89.07 (6)	C1—N1—H2	121.9 (19)
F1 ⁱⁱ —V1—F1	90.93 (6)	H1—N1—H2	118 (3)
F1 ⁱⁱⁱ —V1—F1	180.0	C1—N2—H3	118.1 (19)
F1 ^{iv} —V1—F1	90.93 (6)	C1—N2—H4	118 (2)
F1 ^v —V1—F1	89.07 (6)	H3—N2—H4	124 (3)
F2 ^{vi} —V2—F2 ^{vii}	90.86 (6)	C1—N3—H5	119 (2)
F2 ^{vi} —V2—F2 ^{viii}	89.14 (6)	C1—N3—H6	122 (2)
F2 ^{vii} —V2—F2 ^{viii}	180.00 (8)	H5—N3—H6	117 (3)
F2 ^{vi} —V2—F2 ^{ix}	90.86 (6)	N3—C1—N2	121.1 (3)
F2 ^{vii} —V2—F2 ^{ix}	89.14 (6)	N3—C1—N1	119.7 (2)
F2 ^{viii} —V2—F2 ^{ix}	90.86 (6)	N2—C1—N1	119.1 (2)

Symmetry codes: (i) $-z, -x, -y$; (ii) z, x, y ; (iii) $-x, -y, -z$; (iv) y, z, x ; (v) $-y, -z, -x$; (vi) $-y, z-1/2, -x+1/2$; (vii) $z-1/2, x, -y+1/2$; (viii) $-z+1/2, -x, y+1/2$; (ix) $-x, -y, -z+1$; (x) $y, -z+1/2, x+1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots F2 ^{xi}	0.85 (3)	2.16 (3)	2.906 (3)	147 (3)
N1—H2 \cdots F1 ^{xi}	0.86 (3)	2.12 (3)	2.876 (3)	146 (3)
N2—H3 \cdots F2 ^{iv}	0.89 (4)	2.03 (4)	2.879 (3)	159 (3)
N2—H4 \cdots F1	0.78 (3)	2.08 (3)	2.820 (3)	160 (3)
N3—H5 \cdots F1 ^x	0.84 (4)	2.13 (4)	2.919 (3)	157 (3)
N3—H6 \cdots F2	0.77 (3)	2.09 (3)	2.846 (3)	169 (3)

Symmetry codes: (iv) y, z, x ; (x) $y, -z+1/2, x+1/2$; (xi) $-x, y+1/2, -z+1/2$.