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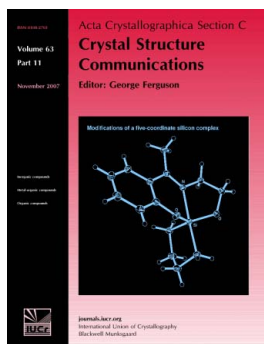
## (OC-6-13)-Difluoridooxidobis(propan-2-ol)(propan-2-olato)vanadium(V)

**Julia Kohl and Dennis Wiedemann***Acta Cryst.* (2013). **C69**, 1482–1484

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## (OC-6-13)-Difluoridooxidobis(propan-2-ol)(propan-2-olato)vanadium(V)

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The distorted octahedral title complex,  $[\text{V}^{\text{V}}(\text{C}_3\text{H}_7\text{O})(\text{C}_3\text{H}_8\text{O})_2\text{F}_2\text{O}]$ , was synthesized *via* ligand exchange at  $[\text{V}^{\text{V}}\text{O}(\text{OiPr})_3]$  with aqueous hydrogen fluoride in propan-2-ol and crystallized from (D)chloroform at 238 K after a few weeks. Crystal structure determination shows two  $C_1$ -symmetric moieties to be present in the asymmetric unit, forming infinite chains along [100] *via* hydrogen bonds. The compound provides the first crystal structure containing the  $[\text{VF}_2\text{O}(\text{OiPr})]$  motif.

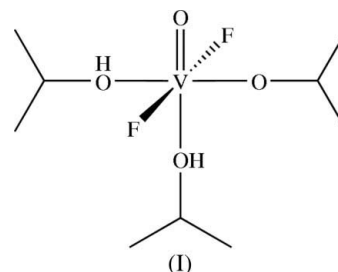
**Keywords:** crystal structure; vanadium complexes; alcoholates; hydrogen fluoride; hydrogen bonds.

### 1. Introduction

The chemistry of precursors for inorganic materials has raised considerable interest in recent years, especially with respect to application in electrodes, optical coatings, and nanomaterials (Avvakumov *et al.*, 2000). The need for soluble or vaporizable compounds has made molecular metal complexes one of the preferred target–substance classes. Exact knowledge of precursor structure is vital for a deeper understanding of deposition, decomposition and optimization potential. Vanadium oxide fluorides – and corresponding lithium compounds – are promising candidates for application as electrode materials in lithium-ion batteries (Mäntymäki *et al.*, 2012). This is based on the fact that theoretical calculations have predicted an increased redox potential through substitution of oxygen with fluorine (Koyama *et al.*, 2000).

We herein describe (OC-6-13)-difluoridooxidobis(propan-2-ol)(propan-2-olato)vanadium(V),  $[\text{V}^{\text{V}}\text{F}_2\text{O}(\text{OiPr})(\text{iPrOH})_2]$ , (I) (see Scheme; the mirror plane in the case of a time-averaged solution structure with ligands freely rotating around the V–O axes is identical with the paper plane), which was discovered serendipitously while synthesizing vanadium-oxide-fluoride precursors from oxidotrīs(propan-2-olato)vanadium(V),  $[\text{VO}(\text{OiPr})_3]$ . Complex (I) is a propan-2-ol adduct of  $[\text{V}^{\text{V}}\text{F}_2\text{O}(\text{OiPr})]$ , a compound already described in the literature (Pribsch & Rehder, 1985). Although the latter is easily prepared, no crystal structure of  $[\text{VF}_2\text{O}(\text{OiPr})]$  or a

compound containing this structure motif has been described so far. Roughly similar coordination environments around vanadium are, however, found in some polynuclear  $\mu$ -pivalato or  $\mu$ -methanolato complexes like  $(\text{Et}_2\text{H}_2\text{N})[\text{Cr}^{\text{III}}_6(\text{V}^{\text{IV}}\text{O})_2\text{F}_8(\text{OOCMe}_3)_{15}]$  (Larsen *et al.*, 2003) and  $(n\text{Bu}_4\text{N})_2[\text{V}^{\text{IV}}_8\text{O}_8(\text{OMe})_{16}(\text{V}^{\text{IV}}\text{OF}_4)]$  (Spandl *et al.*, 2003).



### 2. Experimental

#### 2.1. Synthesis and crystallization

All chemicals, except for  $[\text{VO}(\text{OiPr})_3]$  supplied by Strem Chemicals, were purchased from Sigma–Aldrich and used without further purification.

$[\text{VO}(\text{OiPr})_3]$  (1.70 g, 0.694 mol) was dissolved in propan-2-ol (20 ml). To the resulting colorless solution, aqueous hydrofluoric acid (40%, 0.3 ml, 0.7 mol) was added. The yellow solution obtained was stirred for 90 min at room temperature, the color changing to orange. The solvent was evaporated in a medium vacuum, leaving an orange liquid (*ca* 5 ml).

A sample for NMR spectroscopy was prepared from the product (I) (0.01 ml) and (D)chloroform (0.05 ml). After measurement, the sample was stored at 238 K in the dark and produced clear yellow needles after a few weeks.

NMR spectra were recorded on a Bruker ARV 400 at room temperature. Chemical shifts refer to  $\text{SiMe}_4$ ,  $\text{CCl}_3\text{F}$ , and  $\text{VOCl}_3$  for  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{51}\text{V}$ , respectively. They were calibrated with respect to the residual proton signal for  $^1\text{H}$  ( $\delta = 7.26$ ) or an electronically stored frequency for the other nuclei. The  $^1\text{H}$  NMR signal for the hydroxy H atoms was very broad; its integral suffers from problems of limit choice and thus seems too small.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.08 (*s*, 3H, CH), 3.06 (*s*, 1H, OH), 1.39–1.37 (*m*, 18H,  $\text{CH}_3$ );  $^{19}\text{F}\{^1\text{H}\}$  NMR (188 MHz,  $\text{CDCl}_3$ ):  $\delta$  43.6 (*br m*);  $^{51}\text{V}\{^1\text{H}\}$  NMR (105 MHz,  $\text{CDCl}_3$ ):  $\delta$  –640 (*br m*).

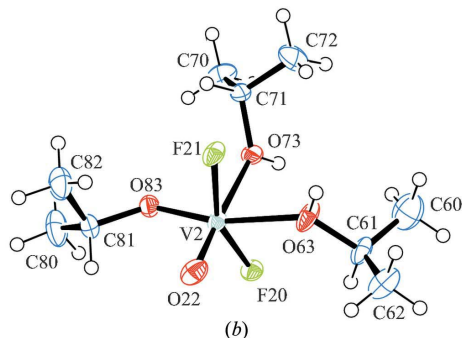
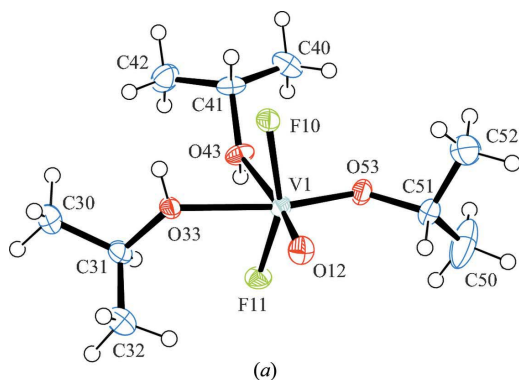
#### 2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located on difference Fourier maps. C-bound H atoms were constrained using a riding model [ $\text{C}–\text{H} = 0.98 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl groups, and  $\text{C}–\text{H} = 1.00 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for methine groups]. Methyl groups were considered rigid but freely rotating. O-bound H atoms were refined with restrained 1,2- [ $\text{O}–\text{H} = 0.84$  (2)  $\text{ \AA}$ , final range: 0.78 (2)–0.81 (5)  $\text{ \AA}$ ] and 1,3-distances [ $\text{C}–\text{H} =$

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	[V(C <sub>3</sub> H <sub>7</sub> O)(C <sub>3</sub> H <sub>8</sub> O) <sub>2</sub> F <sub>2</sub> O]
<i>M<sub>r</sub></i>	284.21
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.0943 (9), 9.9151 (8), 16.4279 (13)
$\alpha$ , $\beta$ , $\gamma$ (°)	97.315 (7), 97.690 (7), 92.324 (7)
<i>V</i> (Å <sup>3</sup> )	1453.5 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.70
Crystal size (mm)	0.89 × 0.20 × 0.14
Data collection	
Diffractometer	Agilent Xcalibur diffractometer
Absorption correction	Analytical [ <i>CrysAlis PRO</i> (Agilent, 2012), based on expressions derived by Clark & Reid (1995)]
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.727, 0.920
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	10818, 5702, 4505
<i>R<sub>int</sub></i>	0.045
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.617
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.052, 0.107, 1.05
No. of reflections	5702
No. of parameters	313
No. of restraints	8
H-atom treatment	H-atom parameters constrained for H on C, refined H-atom coordinates only for H on heteroatoms
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.44, -0.53

Computer programs: *CrysAlis PRO* (Agilent, 2012), *SHELXS2013* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012), *WinGX* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008), *PLATON* (Spek, 2009) and CSM website (Zayit *et al.*, 2011).

**Figure 1**

A view of the two molecules in the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn with an arbitrary radius. Moieties (a) and (b) are in different orientations.

**Table 2**  
Selected geometric parameters (Å, °).

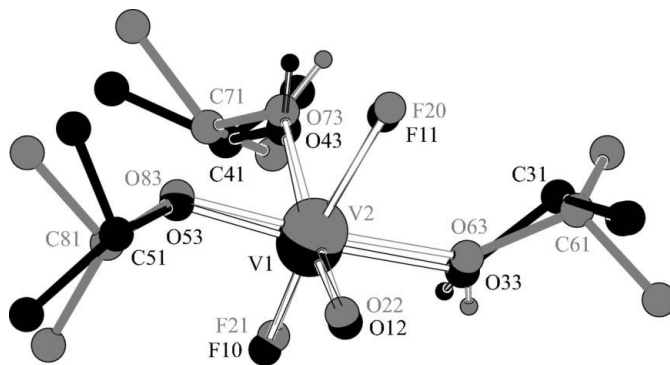
O12–V1	1.581 (2)	O22–V2	1.586 (2)
O33–V1	2.178 (2)	O63–V2	2.139 (2)
O43–V1	2.2513 (19)	O73–V2	2.253 (2)
O53–V1	1.747 (2)	O83–V2	1.754 (2)
F10–V1	1.8423 (14)	F20–V2	1.8391 (14)
F11–V1	1.8424 (15)	F21–V2	1.8578 (15)
O12–V1–O53	99.80 (10)	O22–V2–O83	98.83 (11)
O12–V1–F10	99.20 (9)	O22–V2–F20	98.47 (9)
O53–V1–F10	97.45 (8)	O83–V2–F20	100.51 (8)
O12–V1–F11	98.62 (9)	O22–V2–F21	98.67 (9)
O53–V1–F11	97.01 (8)	O83–V2–F21	95.14 (8)
F10–V1–F11	154.73 (7)	F20–V2–F21	154.66 (8)
O12–V1–O33	94.30 (10)	O22–V2–O63	96.21 (11)
O53–V1–O33	165.77 (9)	O83–V2–O63	164.06 (10)
F10–V1–O33	78.23 (7)	F20–V2–O63	82.38 (7)
F11–V1–O33	82.71 (7)	F21–V2–O63	77.34 (7)
O12–V1–O43	172.37 (10)	O22–V2–O73	177.56 (9)
O53–V1–O43	87.31 (9)	O83–V2–O73	83.05 (9)
F10–V1–O43	82.49 (7)	F20–V2–O73	79.61 (7)
F11–V1–O43	77.61 (7)	F21–V2–O73	82.67 (7)
O33–V1–O43	78.72 (8)	O63–V2–O73	82.07 (9)

1.86 (4) Å, final range: 1.85 (2)–1.90 (3) Å], as well as constrained displacement parameters [*U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(O)].

### 3. Results and discussion

Experiments to synthesize precursors for the preparation of vanadium oxide fluorides were performed with [VO(OiPr)<sub>3</sub>]. It was reacted with different amounts of hydrofluoric acid in organic solvents, giving air- and light-sensitive products. Single crystals of the title compound, (I), were obtained *via* reaction of [VO(OiPr)<sub>3</sub>] with aqueous hydrofluoric acid in propan-2-ol (V–HF–H<sub>2</sub>O = 3:3:5). They formed by recrystallization from (D)chloroform in the refrigerator over a period of a few weeks.

The electroneutral complex (I) crystallized in the triclinic space group *P* $\bar{1}$  with two molecules in the asymmetric unit (Fig. 1). Coordinative V–O bond lengths (Table 2) fall in the common range for vanadium alcoholates, the bonds to the propan-2-olate ligands being by 0.4–0.5 Å shorter than those to the propan-2-ol ligands (Spandl *et al.*, 2000). Furthermore,

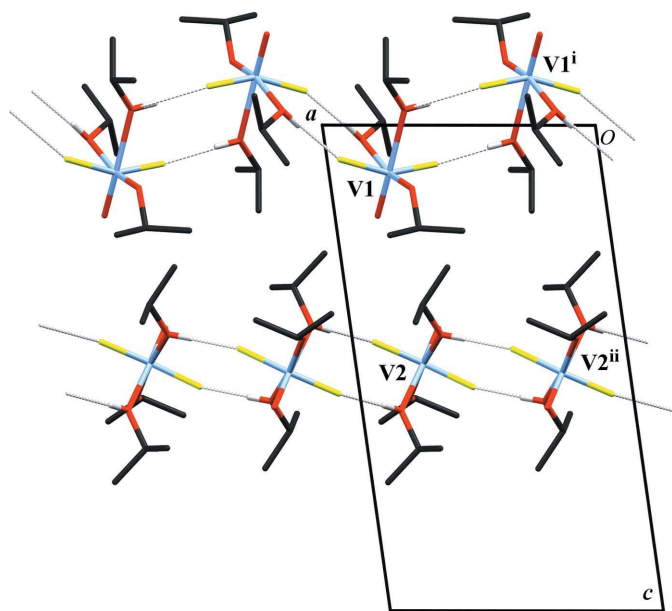
**Figure 2**

Superposition of the two molecules in the asymmetric unit. The moiety containing V2 (grey) has been inverted. Atoms are drawn with arbitrary radii and C-bound H atoms have been omitted for clarity.

**Table 3**  
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O33—H33 $\cdots$ F10 <sup>i</sup>	0.78 (2)	1.90 (2)	2.674 (2)	171 (3)
O43—H43 $\cdots$ F11 <sup>ii</sup>	0.80 (2)	1.90 (2)	2.690 (2)	168 (3)
O63—H63 $\cdots$ F21 <sup>iii</sup>	0.81 (2)	1.85 (2)	2.655 (3)	175 (4)
O73—H73 $\cdots$ F20 <sup>iv</sup>	0.80 (2)	1.97 (2)	2.765 (2)	175 (3)

Symmetry codes: (i)  $-x+2, -y, -z$ ; (ii)  $-x+1, -y, -z$ ; (iii)  $-x+1, -y+1, -z+1$ ; (iv)  $-x+2, -y+1, -z+1$ .



**Figure 3**  
Hydrogen bonds (grey lines) forming infinite chains in (I), viewed along [010]. [Symmetry codes: (i)  $-x+1, -y, -z$ ; (ii)  $-x+1, -y+1, -z+1$ .]

the *trans* effect caused by the strong oxido donor results in an elongation of the opposing bond to a propan-2-ol ligand compared to the other (0.07 Å for V1—O43 and 0.11 Å for V2—O73). The coordination angles (Table 2) differ notably from the ideal values of 90° (*cis*) and 180° (*trans*) for an undistorted octahedron. The continuous symmetry measure (CSM), which ‘quantifies the minimal distance movement that the points of an object have to undergo in order to be transformed into a shape of the desired symmetry’ (Zabrodsky *et al.*, 1992), corroborates this view: with  $S(O_h) = 0.84$  and 0.97 (moieties containing V1 and V2, respectively), the deviation is considerable for a complex of only monodentate ligands.

In the distorted octahedron, the propan-2-ol ligands adopt a *cis* configuration in plane with the oxide and propan-2-olato ligands. The fluoride ligands are *trans*-coordinated in apical

positions with respect to this plane. In solution, this configuration would lead to an achiral molecule in the time average (see Scheme) because of the ligands freely rotating around the V—O axes. As this is not the case in the crystal, a considerable degree of chirality is found in the complex moieties, as defined by continuous chirality measures (CCM):  $S(C_s) = 2.93$  and  $S(C_s) = 3.99$  for the moiety containing V1 and V2, respectively (Zabrodsky & Avnir, 1995). In the chosen asymmetric unit, the two molecules in the asymmetric unit are of opposite chirality sense; an element of pseudosymmetry was not found. In addition, all organic ligands are twisted around the O—C axis with respect to the other moiety (Fig. 3), making the molecules pseudo-enantiomeric.

Each molecule takes part in four intermolecular O—H $\cdots$ F hydrogen bonds. Two neighboring moieties – crystallographically identical to the central hydrogen bond – are each connected by donating and accepting one bond (Table 3). In this manner, infinite chains of (I) propagate along [100] (Fig. 3). These interact *via* van der Waals forces by means of the alkyl residues.

The authors thank Ms Paula Nixdorf for collecting the diffraction data.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3138). Services for accessing these data are described at the back of the journal.

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supplementary materials

*Acta Cryst.* (2013). C69, 1482-1484 [doi:10.1107/S0108270113029776]

**(OC-6-13)-Difluoridooxidobis(propan-2-ol)(propan-2-olato)vanadium(V)**

**Julia Kohl and Dennis Wiedemann**

**Computing details**

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis PRO* (Agilent, 2012); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008), *PLATON/MOLFIT* (Spek, 2009), *PLATON/PLUTON* (Spek, 2009) and CSM website (Zayit *et al.*, 2011).

**(OC-6-13)-Difluoridooxidobis(propan-2-ol)(propan-2-olato)vanadium(V)**

*Crystal data*

[V(C<sub>3</sub>H<sub>7</sub>O)F<sub>2</sub>O(C<sub>3</sub>H<sub>8</sub>O)<sub>2</sub>]

$M_r = 284.21$

Triclinic,  $P\bar{1}$

$a = 9.0943$  (9) Å

$b = 9.9151$  (8) Å

$c = 16.4279$  (13) Å

$\alpha = 97.315$  (7)°

$\beta = 97.690$  (7)°

$\gamma = 92.324$  (7)°

$V = 1453.5$  (2) Å<sup>3</sup>

$Z = 4$

$F(000) = 600$

$D_x = 1.299$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2615 reflections

$\theta = 3.5\text{--}32.6^\circ$

$\mu = 0.70$  mm<sup>-1</sup>

$T = 150$  K

Coloumn, clear yellow

$0.89 \times 0.20 \times 0.14$  mm

*Data collection*

Agilent Xcalibur  
diffractometer

Radiation source: fine-focus sealed tube,  
Agilent Enhance

Graphite monochromator

Detector resolution: 16.3031 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: analytical  
[*CrysAlis PRO* (Agilent, 2012), based on  
expressions derived by Clark & Reid (1995)]

$T_{\min} = 0.727$ ,  $T_{\max} = 0.920$

10818 measured reflections

5702 independent reflections

4505 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$

$\theta_{\max} = 26.0^\circ$ ,  $\theta_{\min} = 3.5^\circ$

$h = -11 \rightarrow 11$

$k = -12 \rightarrow 11$

$l = -17 \rightarrow 20$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.107$

$S = 1.05$

5702 reflections

313 parameters

8 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: difference Fourier map

Heterozyz

$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.53 \text{ e } \text{\AA}^{-3}$$

*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.

**Refinement.** Oxygen-borne hydrogen atoms were refined with restrained 1,2- and 1,3- distances as given by the `_restr_distance_[]` items. Their  $U_{\text{iso}}$  were constrained to be  $1.2 \times U_{\text{eq}}$  of the bearing atoms.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C30	0.8503 (4)	0.3139 (4)	-0.0785 (2)	0.0415 (9)
H30A	0.9509	0.3527	-0.0568	0.062*
H30B	0.7922	0.3827	-0.1038	0.062*
H30C	0.8560	0.2352	-0.1204	0.062*
C31	0.7763 (3)	0.2691 (3)	-0.00849 (18)	0.0251 (7)
H31	0.6740	0.2291	-0.0309	0.030*
C32	0.7665 (4)	0.3851 (4)	0.0593 (2)	0.0416 (9)
H32A	0.7269	0.3497	0.1056	0.062*
H32B	0.7004	0.4519	0.0377	0.062*
H32C	0.8657	0.4288	0.0787	0.062*
C40	0.6679 (4)	-0.3120 (4)	-0.0916 (2)	0.0432 (9)
H40A	0.6861	-0.3383	-0.0358	0.065*
H40B	0.7073	-0.3796	-0.1307	0.065*
H40C	0.5608	-0.3077	-0.1082	0.065*
C41	0.7441 (3)	-0.1747 (3)	-0.09197 (17)	0.0257 (7)
H41	0.8530	-0.1814	-0.0748	0.031*
C42	0.7232 (4)	-0.1247 (4)	-0.17588 (18)	0.0363 (8)
H42A	0.6171	-0.1158	-0.1935	0.054*
H42B	0.7620	-0.1901	-0.2165	0.054*
H42C	0.7769	-0.0359	-0.1720	0.054*
C50	0.5413 (4)	-0.2150 (5)	0.2175 (2)	0.0653 (15)
H50A	0.4750	-0.1436	0.2029	0.098*
H50B	0.5331	-0.2327	0.2741	0.098*
H50C	0.5131	-0.2985	0.1788	0.098*
C51	0.6989 (3)	-0.1691 (3)	0.21226 (17)	0.0265 (7)
H51	0.7284	-0.0867	0.2540	0.032*
C52	0.8081 (4)	-0.2747 (4)	0.2266 (2)	0.0449 (10)
H52A	0.7798	-0.3562	0.1861	0.067*
H52B	0.8089	-0.2984	0.2827	0.067*
H52C	0.9075	-0.2390	0.2202	0.067*
O12	0.8434 (2)	0.0957 (2)	0.18653 (11)	0.0262 (5)
O33	0.8619 (2)	0.1671 (2)	0.02944 (12)	0.0215 (5)
H33	0.910 (3)	0.128 (3)	-0.0003 (15)	0.026*
O43	0.6905 (2)	-0.0755 (2)	-0.03202 (11)	0.0239 (5)
H43	0.6025 (19)	-0.070 (3)	-0.0444 (16)	0.029*
O53	0.7037 (2)	-0.1323 (2)	0.13039 (11)	0.0236 (5)

F10	0.95277 (16)	-0.05790 (17)	0.07061 (9)	0.0238 (4)
F11	0.60516 (15)	0.09967 (18)	0.07997 (10)	0.0251 (4)
V1	0.78003 (5)	0.01389 (5)	0.09899 (3)	0.01807 (13)
C60	0.7591 (4)	0.2460 (5)	0.4056 (2)	0.0567 (12)
H60A	0.8345	0.2659	0.4548	0.085*
H60B	0.7966	0.1817	0.3640	0.085*
H60C	0.6683	0.2060	0.4212	0.085*
C61	0.7257 (3)	0.3742 (4)	0.37068 (19)	0.0321 (8)
H61	0.8204	0.4141	0.3566	0.039*
C62	0.6148 (4)	0.3516 (4)	0.2929 (2)	0.0488 (11)
H62A	0.5205	0.3132	0.3053	0.073*
H62B	0.6530	0.2883	0.2510	0.073*
H62C	0.5985	0.4387	0.2718	0.073*
C70	0.9422 (3)	0.5670 (4)	0.73560 (19)	0.0399 (9)
H70A	1.0157	0.4988	0.7273	0.060*
H70B	0.9076	0.5630	0.7893	0.060*
H70C	0.9878	0.6579	0.7346	0.060*
C71	0.8115 (3)	0.5382 (3)	0.66699 (17)	0.0241 (7)
H71	0.7383	0.6088	0.6773	0.029*
C72	0.7339 (4)	0.4012 (4)	0.6657 (2)	0.0515 (10)
H72A	0.6529	0.3859	0.6192	0.077*
H72B	0.6934	0.3981	0.7178	0.077*
H72C	0.8049	0.3302	0.6593	0.077*
C80	0.9360 (4)	1.0323 (4)	0.6110 (3)	0.0494 (10)
H80A	0.9445	1.0163	0.6690	0.074*
H80B	0.9271	1.1297	0.6078	0.074*
H80C	1.0246	1.0021	0.5876	0.074*
C81	0.7993 (3)	0.9530 (3)	0.5622 (2)	0.0296 (7)
H81	0.7887	0.9726	0.5036	0.036*
C82	0.6575 (3)	0.9858 (4)	0.5978 (2)	0.0423 (9)
H82A	0.5740	0.9288	0.5653	0.063*
H82B	0.6391	1.0820	0.5956	0.063*
H82C	0.6678	0.9678	0.6555	0.063*
O22	0.6793 (2)	0.7502 (2)	0.41889 (12)	0.0336 (6)
O63	0.6726 (2)	0.4712 (3)	0.43103 (14)	0.0372 (6)
H63	0.593 (2)	0.442 (3)	0.4392 (19)	0.045*
O73	0.8580 (2)	0.5506 (2)	0.58798 (12)	0.0260 (5)
H73	0.918 (3)	0.496 (3)	0.5773 (17)	0.031*
O83	0.8222 (2)	0.8103 (2)	0.56364 (11)	0.0240 (5)
F20	0.92143 (16)	0.62287 (18)	0.44693 (9)	0.0250 (4)
F21	0.58303 (16)	0.63762 (18)	0.53906 (10)	0.0277 (4)
V2	0.75177 (5)	0.67038 (5)	0.49047 (3)	0.02055 (14)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C30	0.050 (2)	0.034 (2)	0.050 (2)	0.0146 (17)	0.0211 (17)	0.0222 (18)
C31	0.0236 (15)	0.0228 (19)	0.0315 (17)	0.0078 (13)	0.0063 (13)	0.0088 (14)
C32	0.055 (2)	0.023 (2)	0.049 (2)	0.0054 (17)	0.0167 (18)	0.0049 (17)
C40	0.055 (2)	0.024 (2)	0.054 (2)	0.0129 (17)	0.0149 (18)	0.0065 (18)

C41	0.0205 (15)	0.029 (2)	0.0268 (16)	0.0079 (13)	0.0045 (12)	-0.0036 (14)
C42	0.0443 (19)	0.035 (2)	0.0290 (18)	-0.0025 (16)	0.0118 (15)	-0.0013 (16)
C50	0.035 (2)	0.116 (5)	0.057 (3)	-0.001 (2)	0.0141 (18)	0.051 (3)
C51	0.0301 (16)	0.030 (2)	0.0209 (15)	0.0016 (14)	0.0077 (13)	0.0069 (14)
C52	0.058 (2)	0.045 (3)	0.0355 (19)	0.0183 (19)	0.0110 (17)	0.0109 (18)
O12	0.0270 (11)	0.0274 (14)	0.0234 (11)	-0.0014 (9)	0.0009 (8)	0.0033 (9)
O33	0.0172 (10)	0.0195 (12)	0.0314 (11)	0.0052 (8)	0.0092 (8)	0.0093 (9)
O43	0.0151 (10)	0.0339 (14)	0.0212 (10)	0.0052 (9)	0.0018 (8)	-0.0024 (9)
O53	0.0284 (11)	0.0240 (13)	0.0199 (10)	-0.0013 (9)	0.0071 (8)	0.0057 (9)
F10	0.0195 (8)	0.0253 (11)	0.0294 (9)	0.0065 (7)	0.0067 (7)	0.0095 (8)
F11	0.0165 (8)	0.0263 (11)	0.0337 (9)	0.0043 (7)	0.0069 (7)	0.0036 (8)
V1	0.0152 (2)	0.0193 (3)	0.0207 (3)	0.00082 (19)	0.00436 (19)	0.0043 (2)
C60	0.052 (2)	0.059 (3)	0.056 (2)	0.019 (2)	0.004 (2)	-0.002 (2)
C61	0.0216 (15)	0.033 (2)	0.0394 (19)	-0.0045 (14)	0.0168 (14)	-0.0148 (16)
C62	0.051 (2)	0.060 (3)	0.0324 (19)	0.012 (2)	0.0068 (17)	-0.0066 (19)
C70	0.0351 (18)	0.055 (3)	0.0322 (18)	0.0092 (17)	0.0117 (15)	0.0058 (17)
C71	0.0263 (15)	0.0231 (18)	0.0259 (16)	0.0037 (13)	0.0123 (13)	0.0050 (13)
C72	0.054 (2)	0.040 (3)	0.064 (3)	-0.0123 (19)	0.025 (2)	0.013 (2)
C80	0.042 (2)	0.024 (2)	0.078 (3)	-0.0068 (16)	0.0098 (19)	-0.006 (2)
C81	0.0373 (18)	0.0179 (19)	0.0348 (18)	0.0023 (14)	0.0090 (14)	0.0038 (14)
C82	0.040 (2)	0.028 (2)	0.060 (2)	0.0085 (16)	0.0119 (17)	0.0023 (18)
O22	0.0333 (12)	0.0422 (16)	0.0239 (11)	0.0092 (11)	0.0013 (9)	-0.0001 (10)
O63	0.0235 (11)	0.0395 (16)	0.0441 (13)	-0.0110 (10)	0.0187 (10)	-0.0225 (11)
O73	0.0278 (11)	0.0255 (14)	0.0296 (11)	0.0101 (9)	0.0160 (9)	0.0071 (10)
O83	0.0247 (10)	0.0200 (13)	0.0275 (11)	0.0000 (9)	0.0064 (8)	0.0011 (9)
F20	0.0202 (8)	0.0280 (11)	0.0276 (9)	-0.0011 (7)	0.0092 (7)	0.0012 (8)
F21	0.0203 (8)	0.0297 (11)	0.0320 (9)	-0.0023 (7)	0.0116 (7)	-0.0073 (8)
V2	0.0173 (2)	0.0216 (3)	0.0223 (3)	0.0003 (2)	0.0054 (2)	-0.0014 (2)

*Geometric parameters (Å, °)*

C30—C31	1.512 (4)	C60—C61	1.486 (5)
C30—H30A	0.9800	C60—H60A	0.9800
C30—H30B	0.9800	C60—H60B	0.9800
C30—H30C	0.9800	C60—H60C	0.9800
C31—O33	1.453 (3)	C61—O63	1.437 (3)
C31—C32	1.510 (4)	C61—C62	1.505 (4)
C31—H31	1.0000	C61—H61	1.0000
C32—H32A	0.9800	C62—H62A	0.9800
C32—H32B	0.9800	C62—H62B	0.9800
C32—H32C	0.9800	C62—H62C	0.9800
C40—C41	1.503 (5)	C70—C71	1.515 (4)
C40—H40A	0.9800	C70—H70A	0.9800
C40—H40B	0.9800	C70—H70B	0.9800
C40—H40C	0.9800	C70—H70C	0.9800
C41—O43	1.448 (3)	C71—O73	1.436 (3)
C41—C42	1.514 (4)	C71—C72	1.502 (5)
C41—H41	1.0000	C71—H71	1.0000
C42—H42A	0.9800	C72—H72A	0.9800
C42—H42B	0.9800	C72—H72B	0.9800



C42—H42C	0.9800	C72—H72C	0.9800
C50—C51	1.503 (4)	C80—C81	1.516 (4)
C50—H50A	0.9800	C80—H80A	0.9800
C50—H50B	0.9800	C80—H80B	0.9800
C50—H50C	0.9800	C80—H80C	0.9800
C51—O53	1.443 (3)	C81—O83	1.441 (4)
C51—C52	1.492 (4)	C81—C82	1.515 (4)
C51—H51	1.0000	C81—H81	1.0000
C52—H52A	0.9800	C82—H82A	0.9800
C52—H52B	0.9800	C82—H82B	0.9800
C52—H52C	0.9800	C82—H82C	0.9800
O12—V1	1.581 (2)	O22—V2	1.586 (2)
O33—V1	2.178 (2)	O63—V2	2.139 (2)
O33—H33	0.778 (16)	O63—H63	0.805 (17)
O43—V1	2.2513 (19)	O73—V2	2.253 (2)
O43—H43	0.804 (16)	O73—H73	0.800 (17)
O53—V1	1.747 (2)	O83—V2	1.754 (2)
F10—V1	1.8423 (14)	F20—V2	1.8391 (14)
F11—V1	1.8424 (15)	F21—V2	1.8578 (15)
C31—C30—H30A	109.5	C61—C60—H60A	109.5
C31—C30—H30B	109.5	C61—C60—H60B	109.5
H30A—C30—H30B	109.5	H60A—C60—H60B	109.5
C31—C30—H30C	109.5	C61—C60—H60C	109.5
H30A—C30—H30C	109.5	H60A—C60—H60C	109.5
H30B—C30—H30C	109.5	H60B—C60—H60C	109.5
O33—C31—C32	106.8 (2)	O63—C61—C60	110.6 (3)
O33—C31—C30	109.9 (2)	O63—C61—C62	109.6 (3)
C32—C31—C30	112.4 (3)	C60—C61—C62	112.8 (3)
O33—C31—H31	109.2	O63—C61—H61	107.9
C32—C31—H31	109.2	C60—C61—H61	107.9
C30—C31—H31	109.2	C62—C61—H61	107.9
C31—C32—H32A	109.5	C61—C62—H62A	109.5
C31—C32—H32B	109.5	C61—C62—H62B	109.5
H32A—C32—H32B	109.5	H62A—C62—H62B	109.5
C31—C32—H32C	109.5	C61—C62—H62C	109.5
H32A—C32—H32C	109.5	H62A—C62—H62C	109.5
H32B—C32—H32C	109.5	H62B—C62—H62C	109.5
C41—C40—H40A	109.5	C71—C70—H70A	109.5
C41—C40—H40B	109.5	C71—C70—H70B	109.5
H40A—C40—H40B	109.5	H70A—C70—H70B	109.5
C41—C40—H40C	109.5	C71—C70—H70C	109.5
H40A—C40—H40C	109.5	H70A—C70—H70C	109.5
H40B—C40—H40C	109.5	H70B—C70—H70C	109.5
O43—C41—C40	109.7 (2)	O73—C71—C72	110.5 (3)
O43—C41—C42	109.0 (3)	O73—C71—C70	110.6 (2)
C40—C41—C42	113.7 (3)	C72—C71—C70	112.5 (3)
O43—C41—H41	108.1	O73—C71—H71	107.7
C40—C41—H41	108.1	C72—C71—H71	107.7

C42—C41—H41	108.1	C70—C71—H71	107.7
C41—C42—H42A	109.5	C71—C72—H72A	109.5
C41—C42—H42B	109.5	C71—C72—H72B	109.5
H42A—C42—H42B	109.5	H72A—C72—H72B	109.5
C41—C42—H42C	109.5	C71—C72—H72C	109.5
H42A—C42—H42C	109.5	H72A—C72—H72C	109.5
H42B—C42—H42C	109.5	H72B—C72—H72C	109.5
C51—C50—H50A	109.5	C81—C80—H80A	109.5
C51—C50—H50B	109.5	C81—C80—H80B	109.5
H50A—C50—H50B	109.5	H80A—C80—H80B	109.5
C51—C50—H50C	109.5	C81—C80—H80C	109.5
H50A—C50—H50C	109.5	H80A—C80—H80C	109.5
H50B—C50—H50C	109.5	H80B—C80—H80C	109.5
O53—C51—C52	108.4 (2)	O83—C81—C80	107.4 (3)
O53—C51—C50	107.8 (2)	O83—C81—C82	108.7 (3)
C52—C51—C50	114.0 (3)	C80—C81—C82	113.2 (3)
O53—C51—H51	108.9	O83—C81—H81	109.2
C52—C51—H51	108.9	C80—C81—H81	109.2
C50—C51—H51	108.9	C82—C81—H81	109.2
C51—C52—H52A	109.5	C81—C82—H82A	109.5
C51—C52—H52B	109.5	C81—C82—H82B	109.5
H52A—C52—H52B	109.5	H82A—C82—H82B	109.5
C51—C52—H52C	109.5	C81—C82—H82C	109.5
H52A—C52—H52C	109.5	H82A—C82—H82C	109.5
H52B—C52—H52C	109.5	H82B—C82—H82C	109.5
C31—O33—V1	126.82 (15)	C61—O63—V2	133.84 (18)
C31—O33—H33	113 (2)	C61—O63—H63	108 (2)
V1—O33—H33	105 (2)	V2—O63—H63	118 (2)
C41—O43—V1	133.21 (16)	C71—O73—V2	126.96 (15)
C41—O43—H43	109 (2)	C71—O73—H73	111 (2)
V1—O43—H43	114.6 (19)	V2—O73—H73	121 (2)
C51—O53—V1	130.57 (19)	C81—O83—V2	129.26 (19)
O12—V1—O53	99.80 (10)	O22—V2—O83	98.83 (11)
O12—V1—F10	99.20 (9)	O22—V2—F20	98.47 (9)
O53—V1—F10	97.45 (8)	O83—V2—F20	100.51 (8)
O12—V1—F11	98.62 (9)	O22—V2—F21	98.67 (9)
O53—V1—F11	97.01 (8)	O83—V2—F21	95.14 (8)
F10—V1—F11	154.73 (7)	F20—V2—F21	154.66 (8)
O12—V1—O33	94.30 (10)	O22—V2—O63	96.21 (11)
O53—V1—O33	165.77 (9)	O83—V2—O63	164.06 (10)
F10—V1—O33	78.23 (7)	F20—V2—O63	82.38 (7)
F11—V1—O33	82.71 (7)	F21—V2—O63	77.34 (7)
O12—V1—O43	172.37 (10)	O22—V2—O73	177.56 (9)
O53—V1—O43	87.31 (9)	O83—V2—O73	83.05 (9)
F10—V1—O43	82.49 (7)	F20—V2—O73	79.61 (7)
F11—V1—O43	77.61 (7)	F21—V2—O73	82.67 (7)
O33—V1—O43	78.72 (8)	O63—V2—O73	82.07 (9)
C32—C31—O33—V1	81.7 (3)	C60—C61—O63—V2	118.6 (3)

C30—C31—O33—V1	-156.1 (2)	C62—C61—O63—V2	-116.6 (3)
C40—C41—O43—V1	98.4 (3)	C72—C71—O73—V2	104.5 (3)
C42—C41—O43—V1	-136.6 (2)	C70—C71—O73—V2	-130.3 (2)
C52—C51—O53—V1	-105.7 (3)	C80—C81—O83—V2	-151.4 (2)
C50—C51—O53—V1	130.4 (3)	C82—C81—O83—V2	85.8 (3)
C51—O53—V1—O12	0.1 (2)	C81—O83—V2—O22	8.3 (2)
C51—O53—V1—F10	100.8 (2)	C81—O83—V2—F20	108.7 (2)
C51—O53—V1—F11	-100.0 (2)	C81—O83—V2—F21	-91.4 (2)
C51—O53—V1—O33	172.1 (3)	C81—O83—V2—O63	-152.2 (3)
C51—O53—V1—O43	-177.1 (2)	C81—O83—V2—O73	-173.3 (2)

Hydrogen-bond geometry (Å, °)

<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>
O33—H33 $\cdots$ F10 <sup>i</sup>	0.78 (2)	1.90 (2)	2.674 (2)	171 (3)
O43—H43 $\cdots$ F11 <sup>ii</sup>	0.80 (2)	1.90 (2)	2.690 (2)	168 (3)
O63—H63 $\cdots$ F21 <sup>iii</sup>	0.81 (2)	1.85 (2)	2.655 (3)	175 (4)
O73—H73 $\cdots$ F20 <sup>iv</sup>	0.80 (2)	1.97 (2)	2.765 (2)	175 (3)

Symmetry codes: (i)  $-x+2, -y, -z$ ; (ii)  $-x+1, -y, -z$ ; (iii)  $-x+1, -y+1, -z+1$ ; (iv)  $-x+2, -y+1, -z+1$ .