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$VF(C_4O_4)(H_2O)_2$: a new layer type of diaquavanadium(III) fluoride squarate

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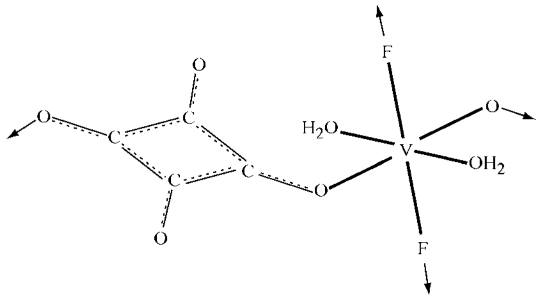
Single crystals of the title compound, poly[diaqua-μ-fluoro-μ-squarato-vanadium(III)], $[V(C_4O_4)F(H_2O)_2]_n$, have been prepared hydrothermally at 423 K. This compound is shown to have a layer-type structure. The V and F atoms are localized on the symmetry centers $2a$ and $2d$, respectively, of the monoclinic system (space group $P2_1/n$) and they form infinite chains which are bridged by the squarate group acting as a bidentate ligand in a *trans* position. Two water molecules complete the octahedral coordination of vanadium(III). The three-dimensionality is ensured by a strong O—H···O hydrogen bond.

Comment

Several metal squarates have been reported. The squarate ligand with its fourfold C=O functionality not only is a potential multiple acceptor of hydrogen bonds but also can be involved either in polydentate (Lee *et al.*, 1996, and references therein; Weiss *et al.*, 1986; Neeraj *et al.*, 2002) or in chelating (Robl & Weiss, 1987; Robl *et al.*, 1987; Trombe *et al.*, 1990) coordination modes depending principally on the metal size and the temperature of formation of the compound. The coordination chemistry of the vanadium squarates is less developed than those of other transition metals. However, original compounds, such as $[V(C_4O_4)(OH)(H_2O)_2]_2 \cdot 2H_2O$ (Brouca-Cabarrecq *et al.*, 2004), $[V(C_4O_4)(OH)(H_2O)]_2$ and $[V(C_4O_4)(OH)]_2 \cdot 4H_2O$ (Lin & Lii, 1997), have been synthesized by the hydrothermal method. These three compounds differ in their respective dimensionalities, *viz.* zero-, two- and three-dimensional, respectively. The first compound is a dimer in which the squarate group exhibits μ_2-coordination in a *cis* position. In the second and third compounds, the squarate group acts as a bridging ligand in μ_3- and μ_4-coordination modes, respectively. Within these compounds, the V atom has an oxidation state of +3, as a result of the powerful reducing property of the squarate ligand under the synthesis conditions.

As part of our continuing investigations of the $V_2O_5/H_2C_4O_4$ system, we have attempted hydrothermal synthesis with this system *via* the fluoride route, using either HF or HBF_4 (see *Experimental*) (Mohanu, 2005). By using the latter fluoride reactant at 423 K for 3 d, a new compound, $[V(C_4O_4)F(H_2O)_2]$, (I), has been isolated as single crystals. This compound crystallizes in the monoclinic system, space group $P2_1/n$. The V and F atoms are localized on the symmetry centers $2a$ and $2d$, respectively, and they form infinite chains running in the x direction (Fig. 1), the V—F distance being 1.8895 (2) Å. To complete the octahedral geometry, each V^{III} site bonds to two squarate O atoms and to two water molecules, at slightly longer distances than the V—F bond length (Table 1). The V^{III} octahedron is quite regular; the angles do not deviate from 90° by more than 3.17°. The V^{III} oxidation state assignment is consistent with a valence sum calculation (Altermatt & Brown, 1985) that gives a value of 3.12, and with the charge requirement of the material. Furthermore, such an oxidation state agrees well with the experimental magnetic moment (2.51 μB, *versus* 2.55 μB for VF_3; Pascal, 1958). These V–F chains are bridged by a squarate ligand in μ_2-coordination in a *trans* position, leading to a layer parallel to the (010) plane. The C—C bond lengths of the squarate ligand are equal within the s.u. values (Table 1), and the corresponding C—C—C angles are within 0.76° of 90°. The slight difference in the C—O bond lengths is a consequence of the fact that atom O1 is only bound to the V atom, while atom O2 is involved only in hydrogen bonds. However, these values are normal for a squarate ligand (Lee *et al.*, 1996), and in particular they indicate a delocalization of the π electrons in the aromatic cycle (West, 1980). Within this layer, adjacent squarate groups are



(I)

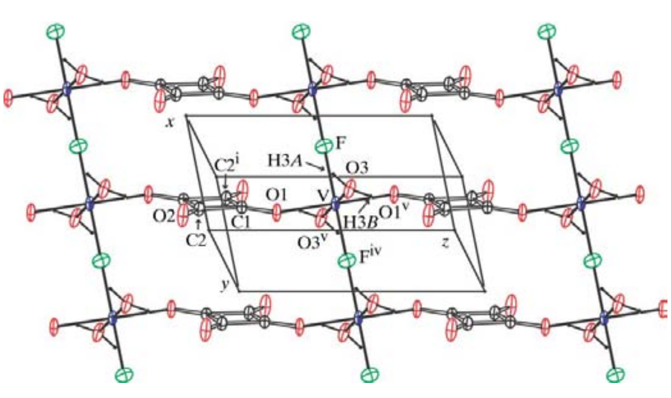


Figure 1
A view, projected on to the (010) plane (slightly inclined), of the structure of (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x + 1, -y + 1, -z$; (iv) $x - 1, y, z$; (v) $-x + 1, -y + 1, -z + 1$.]

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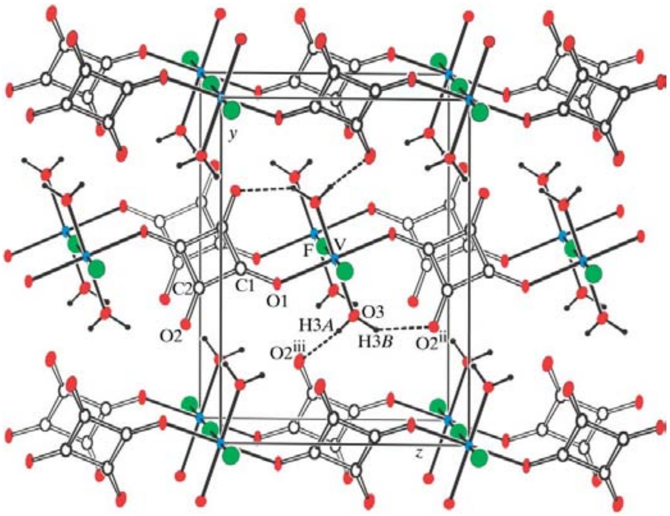

Figure 2
A view, along the x direction, of adjacent layers connected by only hydrogen-bond interactions. [Symmetry codes: (ii) $x, y, z + 1$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.]

parallel and separated by distances of 3.416 (2)–3.7790 (4) Å. Owing to the aromatic character of the squarate species, such distances are indicative of van der Waals interactions in the interval separating two adjacent squarates. These interactions strengthen the cohesion of the layer. The H atoms of the water molecule (O3) participate in two types of strong hydrogen bond towards atoms O2 in different symmetry positions (Fig. 2 and Table 2); the stronger bond, which involves atom H3*A*, relates two adjacent layers, ensuring the three-dimensionality, and the other bond, which involves atom H3*B*, further strengthens the cohesion of the layer. The formula of (I) is similar to $[V(C_4O_4)(OH)(H_2O)_2]_2 \cdot 2H_2O$ (Brouca-Cabarrecq *et al.*, 2004), $[V(C_4O_4)(OH)(H_2O)]_2$ and $[V(C_4O_4)(OH)(C_4O_4)]_2 \cdot 4H_2O$ (Lin & Lii, 1997), with the hydroxy group replaced by a fluoride ion. However, in these three compounds, two V atoms share an edge of the hydroxy groups and their changes of dimensionality (zero-, two- and three-dimensional) are only due to the coordination mode of the squarate ligand (μ_2, μ_3 and μ_4, respectively). This new layered compound is, strictly speaking, a hybrid material, featuring vanadium–fluoride chains connected by an organic ligand.

Experimental

Brown single crystals of the title compound were obtained from an aqueous suspension (5 ml) of V_2O_5 (0.182 g), $H_2C_4O_4$ (0.342 g) and dilute HBF_4 (3 m*M*) in the molar ratio 1:3:3. These reactants were sealed in a Teflon-lined (about 15 ml) steel bomb (autogenous pressure) and heated at 423 K for 3 d. After cooling, the precipitate was filtered off, washed with distilled water and dried at room temperature. The value of the final pH was about 1.0–1.4. The X-ray powder pattern of the whole material was consistent with the theoretical diffractogram of the single crystal. Under the same conditions, using HF leads to the layer $[V(C_4O_4)(OH)(H_2O)]_2$ already reported by Lin & Lii (1997), and a final pH value ranging from 2.5 to 3.0. These pH differences appear a salient factor in the formation of the different phases. The use of HF instead of HBF_4 increases the concentration of OH^- by a factor of about ten. For a high fluoride level, at 473 K for 3 d, the V_2O_5, $H_2C_4O_4$ and HF system in the molar ratio 1:1:6 gives $V_2F_6 \cdot H_2O$ as single crystals, a compound already known (Barthelet *et al.*, 2002).

Crystal data

$[V(C_4O_4)F(H_2O)_2]$
$M_r = 218.01$
Monoclinic, $P2_1/n$
$a = 3.7790$ (4) Å
$b = 11.2070$ (8) Å
$c = 7.8410$ (7) Å
$\beta = 102.019$ (9)°
$V = 324.80$ (5) Å^3
$Z = 2$

$D_x = 2.229$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1121 reflections
$\theta = 6.1$–$32.0°$
$\mu = 1.54$ mm^{-1}
$T = 295$ K
Platelet, brown
$0.60 \times 0.40 \times 0.03$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
ψ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.512$, $T_{max} = 0.956$
5487 measured reflections

1121 independent reflections
709 reflections with $I > 2\sigma(I)$
$R_{int} = 0.080$
$\theta_{max} = 32.0°$
$h = -5 \rightarrow 5$
$k = -16 \rightarrow 16$
$l = -8 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.075$
$S = 0.95$
1121 reflections
58 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

V—F	1.8895 (2)	O2—C2	1.244 (2)
V—O3	1.9687 (14)	C1—C2	1.451 (3)
V—O1	1.9932 (13)	C1—C2^i	1.454 (3)
O1—C1	1.262 (2)		
F—V—O3	89.84 (4)	O1—C1—C2^i	137.68 (19)
F—V—O1	91.02 (4)	C2—C1—C2^i	90.76 (16)
O3—V—O1	86.83 (6)	O2—C2—C1	134.85 (18)
O1—C1—C2	131.56 (18)	O2—C2—C1^i	135.9 (2)

Symmetry code: (i) $-x + 1, -y + 1, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3B···O2^{ii}	0.86	1.94	2.696 (2)	146
O3—H3A···O2^{iii}	0.85	1.82	2.6525 (19)	169

Symmetry codes: (ii) $x, y, z + 1$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

Direct methods associated with *SHELXL97* (Sheldrick, 1997) quickly revealed the sites of heavy atoms, leading to a rough chemical formula $VFO_2(C_4O_4)$. Analysis of the vanadium coordination showed that the charge of the V atom was +3, implying that the electric balance was not ensured. From a difference Fourier synthesis it was then possible to determine two H atoms, localized on a water molecule (O3). The H atoms were placed in positions determined from the difference map, and were allowed to ride on atom O3 with a U_{iso}(H) value equal to $1.2U_{eq}$(O3). Refinement of the positional and anisotropic displacement parameters gave a very good *R* value, the formula $V^{3+}F(C_4O_4)(H_2O)_2$ being well established.

Data collection: *COLLECT* (Nonius 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1268). Services for accessing these data are described at the back of the journal.

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