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Key indicators

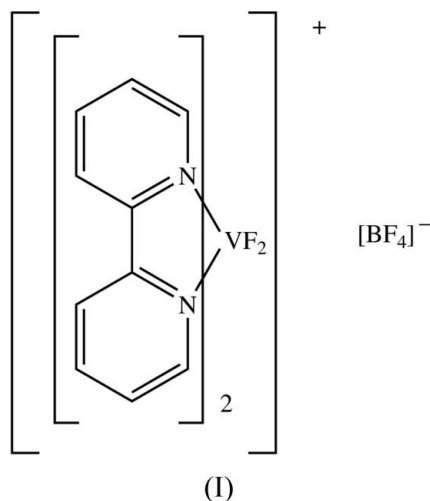
Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.048
 wR factor = 0.133
Data-to-parameter ratio = 15.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Racemic *cis*-bis(2,2'-bipyridyl)difluorovanadium(III)
tetrafluoroborateThe title compound is a salt, $[\text{V}(\text{C}_{10}\text{H}_8\text{N}_2)_2\text{F}_2]^+ \cdot [\text{BF}_4]^-$, in which
pairs of cations, one each of Λ and Δ configuration, are linked
by a centrosymmetric π - π stacking interaction.

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Comment

The title compound, $[\text{V}(\text{bipy})_2\text{F}_2]^+ \cdot [\text{BF}_4]^-$ (bipy is 2,2'-
bipyridyl), (I), was obtained as an adventitious by-product
from the attempted preparation of [bis(2,2'-bipyridyl)(2,4-
pentanedionato-*O,O'*)vanadium(III)] tetrafluoroborate,
 $[\text{V}(\text{bipy})_2(\text{CH}_3\text{COCHCOCH}_3)_3]^+ \cdot [\text{BF}_4]^-$, from tris(2,4-
pentanedionato-*O,O'*)vanadium(III), $[\text{V}(\text{CH}_3\text{COCHCO}-$
 $\text{CH}_3)_3]$. The formation of (I) can be described as the complete
displacement of the ligands in tris(2,4-pentanedionato-
O,O')vanadium(III) and coordination instead of neutral 2,2'-
bipyridyl and of fluoride ions resulting from the adventitious
hydrolysis of part of the tetrafluoroborate component.The cations in (I) are chiral with approximate, but not exact,
local C_2 symmetry. However, the centrosymmetric space group
 $P\bar{1}$ accommodates equal numbers of Λ and Δ enantiomers;
the selected reference cation (Fig. 1) has the Λ configuration.
The individual bond angles (Table 1) around the octahedrally
coordinated metal centre show some considerable deviations
from the ideal values of 90 and 180°, ascribable both to the
rather small bite angles, *ca* 75°, of the bipyridyl ligands, and to
the mutual repulsion of the two F ligands. The V—N bonds
trans to the F ligands are significantly longer than the V—N
bonds *trans* to a bipyridyl N atom.In the two independent bipyridyl ligands, the dihedral
angles between the two ring planes are 3.0 (2) and 8.5 (2)° for
the ligands containing atoms N11 and N31, respectively. The

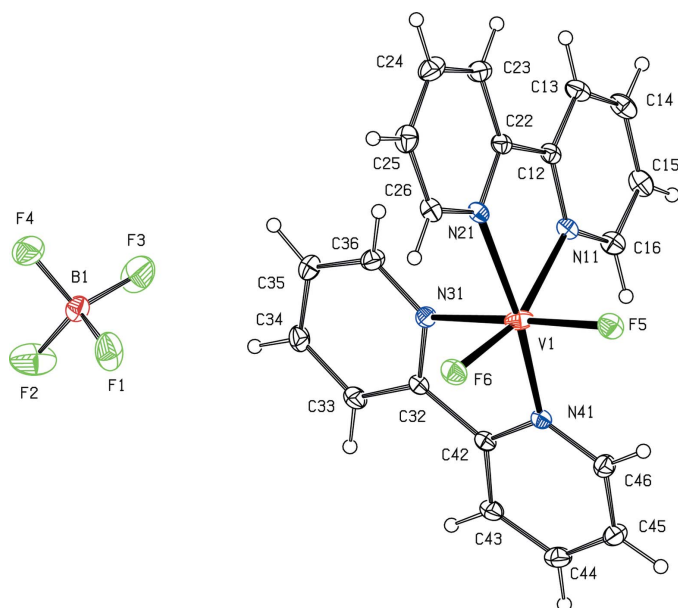


Figure 1
The ionic components of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

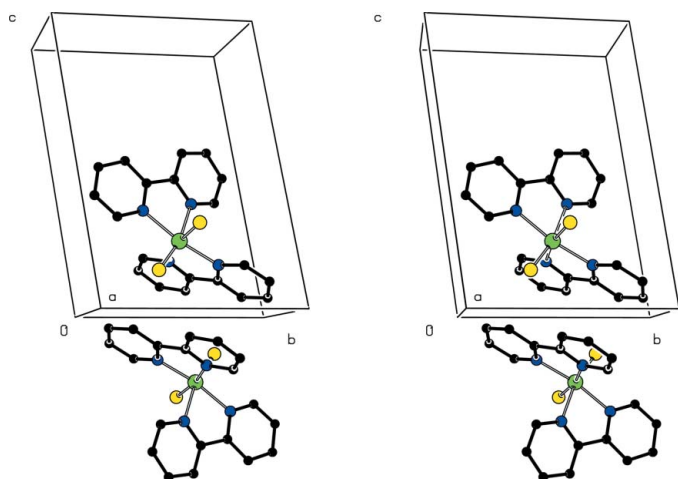


Figure 2
A stereoview of part of the crystal structure of compound (I), showing a pair of enantiomeric cations linked by a π - π stacking interaction. For the sake of clarity, H atoms have been omitted.

chelate ring containing atoms N11 and N21 is effectively planar, but that containing atoms N31 and N41 is distinctly puckered, adopting an envelope conformation with the ring folded across the N31...N41 vector.

The cations are linked into centrosymmetric pairs by means of a single aromatic π - π stacking interaction. The bipyridyl rings N11/C12–C16 at (x, y, z) and N21/C22–C26 at $(1 - x, 1 - y, -z)$ are almost parallel, with a dihedral angle between them of only $3.0(2)^\circ$. The ring-centroid separation is $3.56(2) \text{ \AA}$, and the interplanar spacing is *ca* 3.40 \AA . This interaction thus links a racemic pair of cations across the centre of inversion at $(\frac{1}{2}, \frac{1}{2}, 0)$ (Fig. 2).

There are short C–H...F contacts, both between cations and between cations and anions (Table 2). Although inter-

actions of this type are exceptionally weak (Howard *et al.*, 1996), the concerted effect of cation...anion interactions involving three of the four F atoms in the anion may contribute to the restricted librational motion of the anion, which in simple salts often shows significant evidence for motion and/or disorder.

Experimental

A solution of tris(2,4-pentanedionato-*O,O'*)vanadium(III) (0.3 g) and 2-(2'-pyridyl)pyridinium tetrafluoroborate (0.42 g) in methanol (30 ml) was heated under reflux for 3 h in a dinitrogen atmosphere. After cooling of the reaction mixture, the solvent was removed under reduced pressure to yield the title compound, (I). Red crystals of (I) suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution in acetone (m.p. 488 K, with charring).

Crystal data

$[\text{V}(\text{C}_{10}\text{H}_8\text{N}_2)_2\text{F}_2]\text{BF}_4$
 $M_r = 488.12$
 Triclinic, $P\bar{1}$
 $a = 8.0518(2) \text{ \AA}$
 $b = 9.3238(2) \text{ \AA}$
 $c = 13.5469(3) \text{ \AA}$
 $\alpha = 96.3421(12)^\circ$
 $\beta = 100.2723(14)^\circ$
 $\gamma = 94.9660(13)^\circ$
 $V = 988.70(4) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.640 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 4541 reflections
 $\theta = 3.6\text{--}27.5^\circ$
 $\mu = 0.57 \text{ mm}^{-1}$
 $T = 120(2) \text{ K}$
 Plate, red
 $0.24 \times 0.22 \times 0.04 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\text{min}} = 0.875$, $T_{\text{max}} = 0.977$
 20038 measured reflections

4541 independent reflections
 3970 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -10 \rightarrow 10$
 $k = -12 \rightarrow 12$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.133$
 $S = 1.17$
 4541 reflections
 289 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 0.8934P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.53 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.68 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

V1–N11	2.1823 (19)	V1–N31	2.2247 (19)
V1–N21	2.114 (2)	V1–N41	2.1082 (19)
V1–F5	1.7232 (15)	V1–F6	1.7389 (15)
F5–V1–N11	88.08 (7)	N11–V1–N21	75.01 (7)
F5–V1–N21	99.97 (7)	N11–V1–N31	80.02 (7)
F5–V1–N31	160.97 (8)	N11–V1–N41	98.59 (7)
F5–V1–N41	92.76 (7)	N21–V1–N31	91.30 (7)
F6–V1–N11	160.98 (8)	N21–V1–N41	165.44 (8)
F6–V1–N21	90.18 (7)	N31–V1–N41	74.59 (7)
F6–V1–N31	88.60 (7)	F5–V1–F6	106.51 (7)
F6–V1–N41	92.94 (7)		

Table 2
Geometry of short inter-ion contacts (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C13—H13 \cdots F5 ⁱ	0.95	2.50	3.265 (3)	137
C14—H14 \cdots F5 ⁱⁱ	0.95	2.42	3.145 (3)	133
C16—H16 \cdots F3 ⁱⁱⁱ	0.95	2.50	3.402 (3)	158
C24—H24 \cdots F2 ^{iv}	0.95	2.47	3.279 (4)	143
C33—H33 \cdots F6 ^v	0.95	2.42	3.209 (3)	140
C34—H34 \cdots F1	0.95	2.55	3.227 (3)	129
C43—H43 \cdots F6 ^v	0.95	2.46	3.180 (3)	132

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

All H atoms were located in difference maps and subsequently treated as riding atoms, with C—H distances of 0.95 Å and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97*

(Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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