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Bis[2-(1-methyl-1*H*-imidazol-2-yl-3-iosulfanyl)-6-(1-methyl-1*H*-imidazol-2-ylsulfanyl)pyridine] tetrachloroferrate tetrafluoroborate

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The cations of the title complex, [*H*-{2,6-(meth)$_2$py}]$_2$-[FeCl$_4$][BF$_4$] or ($C_{13}H_{14}N_5S_2$)$_2$[FeCl$_4$]BF$_4$, form dimers of protonated 2,6-bis(1-methyl-1*H*-imidazol-2-ylsulfanyl)-pyridine molecules, which are held together by moderate N—H···N hydrogen bonds.

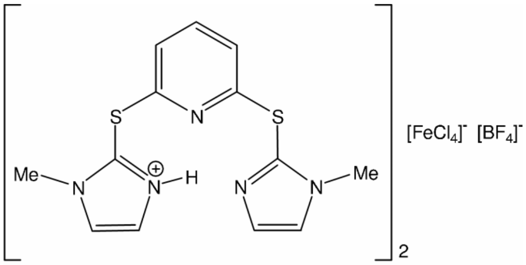
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.006 Å
R factor = 0.049
wR factor = 0.095
Data-to-parameter ratio = 18.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Multidentate nitrogen-donor ligands are highly prevalent in transition-metal coordination chemistry and, with readily accessible synthetic routes, form an extremely large and diverse family of compounds. Consequently, these molecules may be employed in a wide variety of research areas with applications that include homogeneous catalysis, molecular magnetism, photochemistry and liquid crystals, in addition to fundamental research probing the chemistry of biological systems. While investigating the coordination chemistry of tripodal nitrogen-donor ligands, such as 2,6-bis(1-methyl-1*H*-imidazol-2-ylsulfanyl)pyridine [2,6-(meth)$_2$py], the salt [*H*-{2,6-(meth)$_2$py}]$_2$[FeCl$_4$][BF$_4$], (I), was crystallized.



(I)

The structure of (I) comprises two N-protonated 2-(1-methyl-1*H*-imidazol-2-yl-3-iosulfanyl)-6-(1-methyl-1*H*-imidazol-2-ylsulfanyl)pyridine molecules, one tetrachloroferrate and one tetrafluoroborate anion. On each organic moiety, one of the two methimazolyl heterocycles has a protonated imine N atom. Consequently, the cations form a dimer (Fig. 1), held together by moderately strong (Jeffery, 1997) N—H···N hydrogen bonds. Within each cation, the angle at the S atom bridging between the pyridyl and methimazolyl rings prevents the two methimazolyl rings from being coplanar [the angle between the planes is 26.2 (2)° in both molecules in the asymmetric unit]. The torsion of the methimazolyl rings about the C—S bonds appears to be relatively facile, with angles between the 1*H*-imidazol-2-ylsulfanyl and pyridyl ring planes of 75.2 (3), 87.8 (3), 88.6 (3) and 93.4 (3)°. As shown in Fig. 2, the pyridyl rings of dimerized cations are slightly offset, the angle between the two planes being 9.7 (2)°, with a closest

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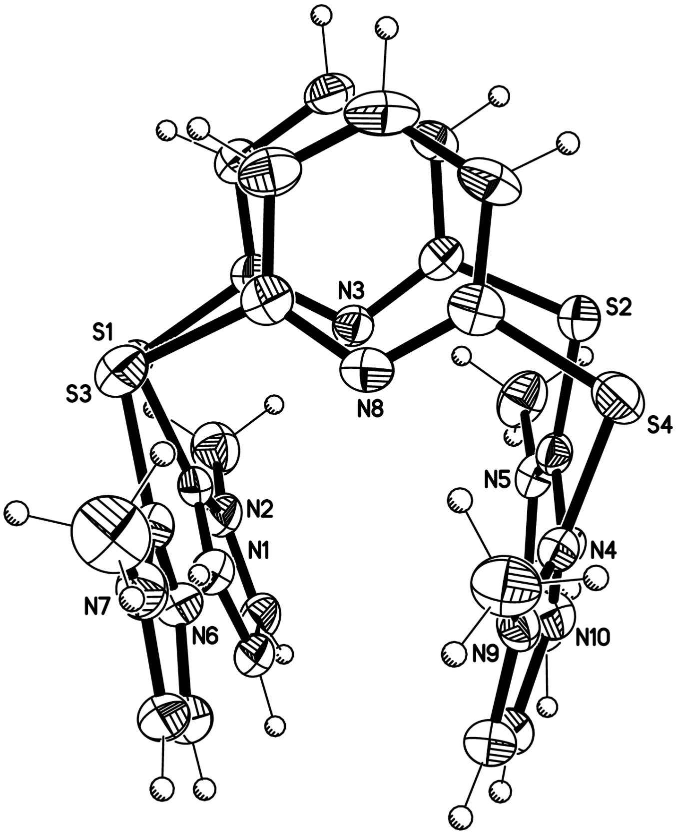

Figure 1
Displacement ellipsoid plot of (I), with atoms represented at the 50% probability level. The anions have been omitted for clarity.

separation between these rings of 3.606 (3) Å (C7 and C20). Thus any $\pi\cdots\pi$ interaction between the pyridyl rings is relatively weak, and is a consequence of the N—H···N hydrogen bonds between the cations.

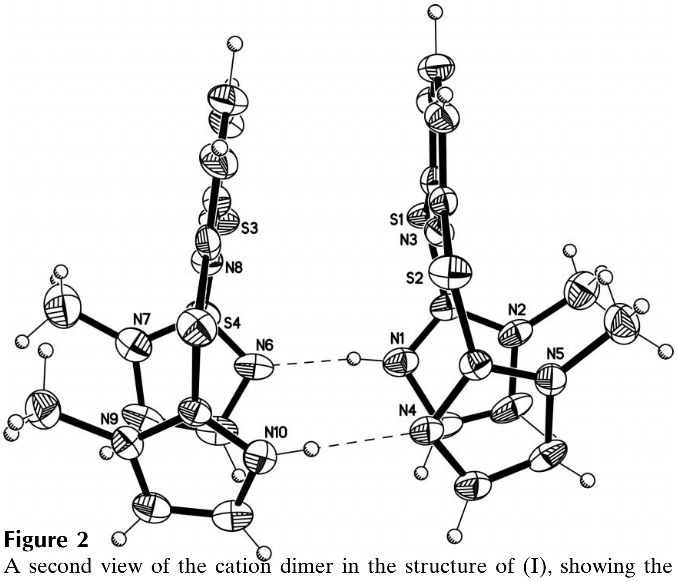

Figure 2
A second view of the cation dimer in the structure of (I), showing the offset face-to-face orientation of the pyridyl rings. Dashed lines indicate the N—H···N hydrogen bonds between the cations.

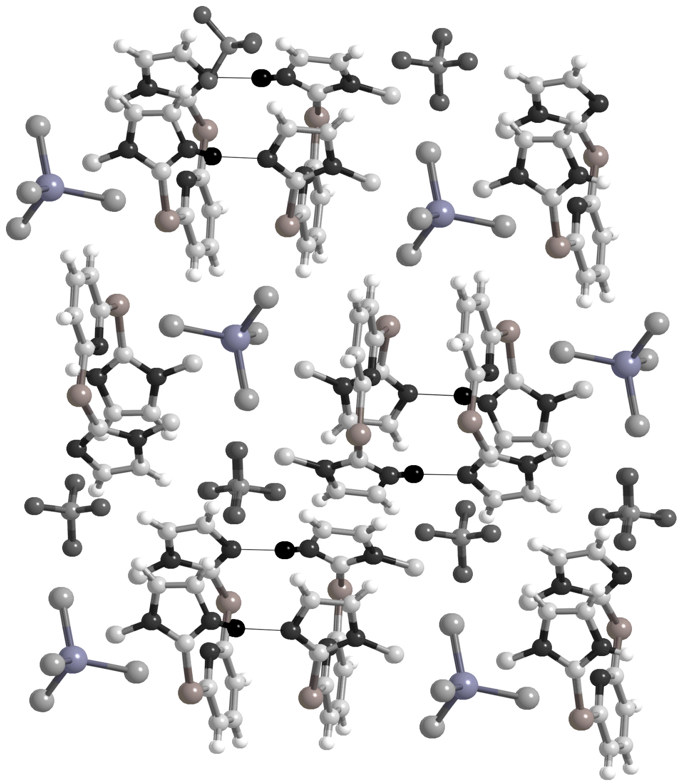

Figure 3
The crystal structure of (I), with the N—H···N hydrogen bonds shown as thin black lines.

In the crystal structure of (I), the cation dimers are separated by both tetrafluoroborate and tetrachloroferrate anions (Fig. 3), with several moderate C—H···F and weak C—H···Cl hydrogen bonds between the ions (Table 2).

Experimental

All reagents were purchased from Aldrich and used as received. All manipulations were carried out under an atmosphere of nitrogen, using dry deoxygenated solvents. A solution of methimazole (2.18 g, 19.1 mmol) in *N,N′*-dimethylformamide (DMF, 30 ml) was added to a suspension of sodium hydride (0.96 g, 24.0 mmol) in DMF (200 ml), and the mixture stirred at room temperature for 2 h. Subsequently, solid 2,6-dichloropyridine (1.46 g, 9.9 mmol) was added, and the mixture heated to reflux for 60 h. On cooling to room temperature, the mixture was poured over ice and the product extracted into CH_2Cl_2. The combined CH_2Cl_2 fractions were dried over $MgSO_4$, filtered and reduced to dryness *in vacuo*, yielding a yellow oil, which was recrystallized from hot ethanol, giving 2,6-bis(1-methyl-1*H*-imidazol-2-ylsulfanyl)pyridine as a pale-yellow solid (2.40 g, 7.9 mmol, 80%). Crystals of (I) suitable for X-ray diffraction studies were grown by allowing diethyl ether vapour to diffuse into an acetone solution containing iron(II) tetrafluoroborate hexahydrate and 2,6-bis(1-methyl-1*H*-imidazol-2-ylsulfanyl)pyridine over a period of 3 d.

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Crystal data

$2C_{13}H_{14}N_5S_2^+ \cdot FeCl_4^- \cdot BF_4^-$
$M_r = 893.28$
Triclinic, $P\overline{1}$
$a = 9.0531$ (10) Å
$b = 13.2213$ (14) Å
$c = 16.0249$ (18) Å
$\alpha = 82.51$ (2)°
$\beta = 82.04$ (3)°
$\gamma = 82.82$ (2)°
$V = 1872.2$ (4) Å^3

$Z = 2$
$D_x = 1.585$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 391 reflections
$\theta = 1.9$–27.6°
$\mu = 0.97$ mm^{-1}
$T = 150$ (2) K
Lath, yellow
0.41 × 0.14 × 0.04 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SAINT*; Bruker, 2001)
$T_{\min} = 0.693$, $T_{\max} = 0.960$
10005 measured reflections

8426 independent reflections
4004 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.047$
$\theta_{\max} = 29.0°$
$h = -12 \rightarrow 10$
$k = -17 \rightarrow 17$
$l = -21 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.095$
$S = 0.89$
8426 reflections
455 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0259P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.011$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—Cl4	2.1864 (12)	Fe1—Cl3	2.1972 (11)
Fe1—Cl1	2.1902 (12)	Fe1—Cl2	2.1983 (11)
C4—S1—C5	101.14 (18)	C17—S3—C18	102.64 (18)
C10—S2—C9	101.97 (17)	C23—S4—C22	100.61 (18)

Table 2
Intermolecular hydrogen bonds (Å, °) in the crystal structure of (I).

D—H$\cdots A$	D—H	$D\cdots A$	D—H$\cdots A$
N1—H1N$\cdots$N6	1.82	2.675 (3)	171
N10—H10N$\cdots$N4	1.88	2.718 (3)	163
C1—H1$A\cdots$F1	2.24	3.154 (3)	143
C25—H25$A\cdots$F3	2.32	3.238 (3)	174
C26—H26$C\cdots$F4	2.34	3.273 (3)	176
C2—H2$A\cdots$F1	2.39	3.241 (3)	173
C24—H24$A\cdots$F3	2.45	3.211 (3)	137
Cl3—H13$B\cdots$Cl3	2.79	3.562 (3)	160

The H atoms of the cation were located in a difference map and constrained to idealized geometries. The methyl groups were allowed to rotate but not to tip.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT* and *SHELXTL* (Bruker, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2001).

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References

Bruker (2001). *SMART* (Version 5.625), *SAINT* (Version 6.02a) and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Jeffery, G. A. (1997). *An Introduction to Hydrogen Bonding*. Oxford University Press.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Spek, A. L. (2001). *PLATON*. University of Utrecht, The Netherlands.

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