



Crystal structure of (1*E*,1'*E*)-1,1'-(pyridine-2,6-di-yl)bis[*N*-(2,3,4,5,6-pentafluorophenyl)ethan-1-imine]

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Keywords: crystal structure; pyridine diimine; redox non-innocent ligand; electron-withdrawing groups; Schiff base.

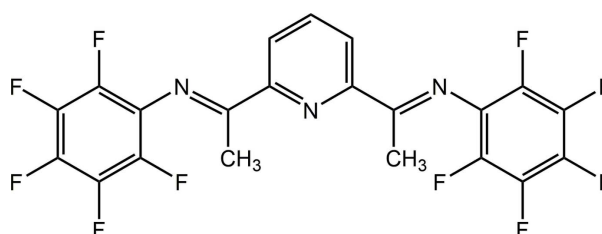
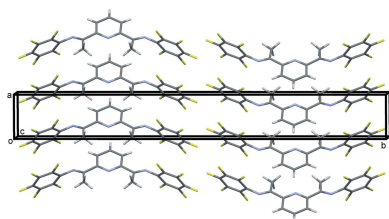
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The title compound, C₂₁H₉F₁₀N₃, represents a potential redox non-innocent pyridine diimine ligand system. It consists of a central pyridine ring with two pentafluorophenyl substituted imine groups in positions 2 and 6. The whole molecule is generated by mirror symmetry, the mirror bisecting the N and *para*-C atom of the pyridine ring. The perfluorophenyl ring is inclined to the pyridine ring by 73.67 (8)°. In the crystal, molecules stack along the *a* axis, but there are no significant intermolecular interactions present.

1. Chemical context

The utilization of non-innocent ligand systems in organometallic chemistry can produce secondary reactivity and can result in unique mechanistic and redox properties (Babbini & Iluc, 2015; Praneeth *et al.*, 2012). Redox non-innocence is generally observed with chelate ligands which possess low-lying π -systems that can allow electron transfer (Lyaskovskyy & de Bruin, 2012). These ligand systems allow multiple-electron redox events to take place on metal centers, which are usually relegated to single-electron events (Haneline & Heyduk, 2006). This is useful for the utilization of benign and economically viable first-row transition metals instead of traditional noble-metal catalysts (Chirik & Wiegardt, 2010). The development of new and varied ligands systems is essential for the understanding of the structure–property relationships, which give rise to redox non-innocence. Given the significance and current interest in redox-active ligand systems, herein we report on the synthesis and crystal structure of a potential redox-active pyridine diimine system containing electron-withdrawing substituents.



2. Structural commentary

The title compound, Fig. 1, crystallizes in the monoclinic space group *P*2₁/*m* with the mirror plane, at (*x*, 0.25, *z*), bisecting the

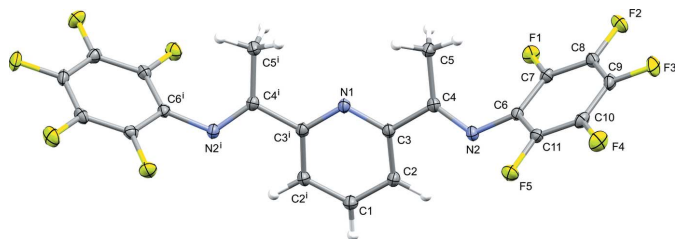


Figure 1

The molecular structure of the title compound, with the atom labelling [symmetry code: (i) $x, -y + \frac{1}{2}, z$]. Displacement ellipsoids are drawn at the 50% probability level.

pyridine N atom, N1, and C atom, C1. Thus, only half of the molecule is present in the asymmetric unit (Fig. 1). The pentafluorophenyl groups are oriented in a *synclinal* fashion with respect to the pyridine ring, with the two rings being inclined to one another by $73.67(6)^\circ$. The imine nitrogen atom, N2, is oriented in an *anti*-conformation with respect to the pyridine nitrogen, N1. This orientation is in contrast with the molecule acting as a tridentate ligand coordinating to the chromium ion in complex trichloro(2,6-bis(1-(pentafluorophenylimino)ethyl)pyridine-*N,N',N''*)chromium(III) acetonitrile monosolvate (Nakayama *et al.*, 2005). Here, the imine N atoms adopt a *syn*-conformation upon coordination to the chromium ion.

3. Supramolecular features

In the crystal, the molecules stack along the *a* axis (Fig. 2). Despite the presence of multiple aromatic rings within the molecule, there are no obvious π -stacking interactions; the phenyl rings are clearly offset. Thus the only intermolecular interactions present are typical van der Waals interactions.

4. Database survey

A search of the Cambridge Structural Database (CSD, V5.38, last update February 2017; Groom *et al.*, 2016) for related structures reveals that the pentafluorophenyl adduct reported here has been reported as a chelating ligand in the chromium complex, trichloro(2,6-bis(1-(pentafluorophenylimino)ethyl)-

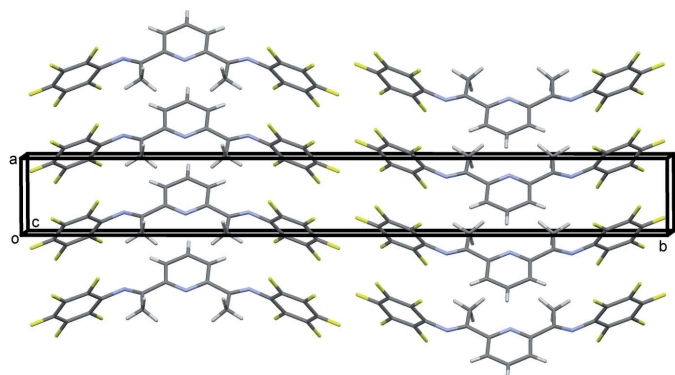


Figure 2

A view along the *c* axis of the crystal packing of the title compound.

Table 1

Experimental details.

Crystal data	
Chemical formula	$C_{21}H_9F_{10}N_3$
M_r	493.31
Crystal system, space group	Monoclinic, $P2_1/m$
Temperature (K)	120
a, b, c (Å)	4.2713 (6), 35.792 (5), 5.9516 (9)
β ($^\circ$)	93.326 (2)
V (Å ³)	908.3 (2)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.18
Crystal size (mm)	0.24 × 0.19 × 0.14
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
T_{\min} , T_{\max}	0.697, 0.729
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13884, 2277, 1989
R_{int}	0.025
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.666
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.088, 1.07
No. of reflections	2277
No. of parameters	158
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.36, -0.19

Computer programs: APEX3 and SAINT (Bruker, 2016), SHELXS97 (Sheldrick, 2008), Mercury (Macrae *et al.*, 2008), SHELXL2016 (Sheldrick, 2015) and publCIF (Westrip, 2010).

pyridine-*N,N',N''*)chromium(III) acetonitrile monosolvate (CSD refcode: BOMROL; Nakayama *et al.*, 2005). The mesityl and 2,6-diisopropylphenyl species are well represented and the solid-state structures of these free molecules have been reported; *viz.* SISYEA (Boyt & Chaplin, 2014) and HORSEM (Yap & Gambarotta, 1999), respectively.

5. Synthesis and crystallization

The reagent 2,6-diacetylpyridine was synthesized by a previously reported method (Su & Feng, 2010), and the ligand was prepared by a modification of a previously reported Schiff-base condensation method (Small & Brookhart, 1999).

A mixture of 2,6-diacetylpyridine (1.0 g, 6.10 mmol), 2,3,4,5,6-pentafluoroaniline (4.07 g, 22.2 mmol) and *p*-toluenesulfonic acid (10 mg, 0.058 mmol) in toluene (100 ml) was refluxed for 30 h during which time water was removed by a Dean–Stark apparatus. The crude yellow product was washed with cold methanol and filtered producing a pure off-white solid (yield 1.65 g, 54.8%). Colorless block-like crystals were obtained by vapor diffusion of hexanes into a saturated dichloromethane solution of the title compound. Spectroscopic data: ¹H NMR (60 MHz, CDCl₃): δ 8.6–7.8 (*m*, 3H, Py-*H*), 2.5 (*s*, 6H, CH₃), and MS (ESI): m/z 494 [C₂₁H₉F₁₀N₃]⁺H⁺.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The hydrogen atoms were included

in calculated positions and refined with a riding model: C–H = 0.95–0.98 Å with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C-methyl})$ and $1.2U_{\text{eq}}(\text{C})$ for other H atoms.

Acknowledgements

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Crystal structure of (1*E*,1'*E*)-1,1'-(pyridine-2,6-diyl)bis[*N*-(2,3,4,5,6-pentafluorophenyl)ethan-1-imine]

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Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINTE* (Bruker, 2016); data reduction: *SAINTE* (Bruker, 2016); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2016* (Sheldrick, 2015) and *publCIF* (Westrip, 2010).

(1*E*,1'*E*)-1,1'-(Pyridine-2,6-diyl)bis[*N*-(2,3,4,5,6-pentafluorophenyl)ethan-1-imine]

Crystal data

C₂₁H₉F₁₀N₃

M_r = 493.31

Monoclinic, *P2₁/m*

a = 4.2713 (6) Å

b = 35.792 (5) Å

c = 5.9516 (9) Å

β = 93.326 (2)°

V = 908.3 (2) Å³

Z = 2

F(000) = 492

D_x = 1.804 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 5126 reflections

θ = 4.6–56.5°

μ = 0.18 mm⁻¹

T = 120 K

Block, colorless

0.24 × 0.19 × 0.14 mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: sealed tube

Graphite monochromator

Detector resolution: 8.33 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

T_{min} = 0.697, *T_{max}* = 0.729

13884 measured reflections

2277 independent reflections

1989 reflections with *I* > 2σ(*I*)

R_{int} = 0.025

θ_{max} = 28.3°, θ_{min} = 2.3°

h = -5→5

k = -47→44

l = -7→7

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.034

wR(*F*²) = 0.088

S = 1.07

2277 reflections

158 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 0.4768P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$$

Special details

Experimental. All other reagents and solvents were purchased commercially and used without further purification. ^1H NMR was collected on a Varian 60 MHz NMR. Mass spectra were collected using direct injection on a ThermoScientific TSQ-ESI Mass spectrometer.

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

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
F1	0.42432 (19)	0.38311 (2)	0.12835 (13)	0.02066 (19)
F2	0.2099 (2)	0.45211 (2)	0.02453 (13)	0.0251 (2)
F3	-0.1849 (2)	0.48751 (2)	0.29875 (14)	0.0261 (2)
F4	-0.3500 (2)	0.45363 (2)	0.68211 (14)	0.0254 (2)
F5	-0.13051 (19)	0.38487 (2)	0.79035 (13)	0.02134 (19)
N1	0.2566 (4)	0.250000	0.4081 (2)	0.0138 (3)
N2	0.2674 (3)	0.34658 (3)	0.52933 (17)	0.0155 (2)
C1	0.6985 (4)	0.250000	0.7721 (3)	0.0178 (4)
H1	0.855045	0.250001	0.892210	0.021*
C2	0.5833 (3)	0.28342 (3)	0.6836 (2)	0.0160 (3)
H2	0.653646	0.306655	0.745044	0.019*
C3	0.3612 (3)	0.28213 (3)	0.5019 (2)	0.0139 (2)
C4	0.2187 (3)	0.31743 (3)	0.4075 (2)	0.0138 (2)
C5	0.0259 (3)	0.31505 (4)	0.1893 (2)	0.0179 (3)
H5A	-0.093139	0.338255	0.165094	0.027*
H5B	-0.119674	0.293945	0.194596	0.027*
H5C	0.164407	0.311399	0.065501	0.027*
C6	0.1457 (3)	0.38157 (3)	0.4594 (2)	0.0137 (2)
C7	0.2293 (3)	0.39993 (3)	0.2659 (2)	0.0149 (2)
C8	0.1229 (3)	0.43548 (4)	0.2117 (2)	0.0165 (3)
C9	-0.0740 (3)	0.45357 (3)	0.3516 (2)	0.0175 (3)
C10	-0.1585 (3)	0.43632 (4)	0.5469 (2)	0.0170 (3)
C11	-0.0465 (3)	0.40098 (3)	0.5999 (2)	0.0150 (2)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0216 (4)	0.0202 (4)	0.0210 (4)	0.0031 (3)	0.0075 (3)	-0.0019 (3)
F2	0.0339 (5)	0.0204 (4)	0.0213 (4)	-0.0026 (3)	0.0040 (3)	0.0081 (3)
F3	0.0326 (5)	0.0118 (4)	0.0330 (5)	0.0066 (3)	-0.0043 (4)	0.0023 (3)
F4	0.0243 (4)	0.0242 (4)	0.0284 (4)	0.0077 (3)	0.0070 (3)	-0.0070 (3)
F5	0.0270 (4)	0.0210 (4)	0.0164 (4)	-0.0022 (3)	0.0053 (3)	0.0018 (3)
N1	0.0163 (7)	0.0099 (7)	0.0152 (7)	0.000	0.0013 (5)	0.000

N2	0.0183 (5)	0.0106 (5)	0.0173 (5)	0.0005 (4)	-0.0009 (4)	0.0007 (4)
C1	0.0199 (9)	0.0156 (8)	0.0174 (8)	0.000	-0.0037 (7)	0.000
C2	0.0193 (6)	0.0112 (6)	0.0172 (6)	-0.0009 (4)	-0.0007 (5)	-0.0010 (4)
C3	0.0155 (6)	0.0116 (6)	0.0146 (5)	-0.0004 (4)	0.0019 (4)	0.0005 (4)
C4	0.0145 (6)	0.0120 (5)	0.0150 (5)	-0.0003 (4)	0.0011 (4)	0.0008 (4)
C5	0.0225 (7)	0.0134 (6)	0.0172 (6)	0.0009 (5)	-0.0040 (5)	-0.0010 (4)
C6	0.0145 (6)	0.0105 (5)	0.0156 (6)	-0.0001 (4)	-0.0026 (4)	-0.0009 (4)
C7	0.0146 (6)	0.0138 (6)	0.0163 (6)	0.0003 (4)	0.0013 (4)	-0.0027 (4)
C8	0.0182 (6)	0.0146 (6)	0.0166 (6)	-0.0026 (5)	-0.0004 (5)	0.0031 (5)
C9	0.0188 (6)	0.0097 (5)	0.0234 (6)	0.0014 (5)	-0.0045 (5)	-0.0003 (5)
C10	0.0153 (6)	0.0160 (6)	0.0196 (6)	0.0020 (5)	0.0008 (5)	-0.0053 (5)
C11	0.0164 (6)	0.0146 (6)	0.0137 (5)	-0.0034 (5)	-0.0001 (4)	-0.0003 (4)

Geometric parameters (Å, °)

F1—C7	1.3439 (14)	C2—H2	0.9500
F2—C8	1.3348 (15)	C3—C4	1.4974 (16)
F3—C9	1.3347 (14)	C4—C5	1.4995 (17)
F4—C10	1.3330 (15)	C5—H5A	0.9800
F5—C11	1.3391 (14)	C5—H5B	0.9800
N1—C3 ⁱ	1.3432 (14)	C5—H5C	0.9800
N1—C3	1.3432 (14)	C6—C7	1.3902 (17)
N2—C4	1.2806 (16)	C6—C11	1.3913 (17)
N2—C6	1.4098 (15)	C7—C8	1.3829 (18)
C1—C2	1.3857 (15)	C8—C9	1.3787 (19)
C1—C2 ⁱ	1.3858 (15)	C9—C10	1.3822 (19)
C1—H1	0.9500	C10—C11	1.3824 (18)
C2—C3	1.3976 (17)		
C3 ⁱ —N1—C3	117.76 (15)	H5B—C5—H5C	109.5
C4—N2—C6	120.78 (10)	C7—C6—C11	116.79 (11)
C2—C1—C2 ⁱ	119.37 (16)	C7—C6—N2	123.82 (11)
C2—C1—H1	120.3	C11—C6—N2	119.10 (11)
C2 ⁱ —C1—H1	120.3	F1—C7—C8	118.50 (11)
C1—C2—C3	118.40 (12)	F1—C7—C6	119.40 (11)
C1—C2—H2	120.8	C8—C7—C6	122.09 (12)
C3—C2—H2	120.8	F2—C8—C9	120.24 (11)
N1—C3—C2	122.98 (11)	F2—C8—C7	120.09 (12)
N1—C3—C4	116.64 (11)	C9—C8—C7	119.67 (12)
C2—C3—C4	120.35 (11)	F3—C9—C8	120.38 (12)
N2—C4—C3	115.20 (11)	F3—C9—C10	119.88 (12)
N2—C4—C5	126.84 (11)	C8—C9—C10	119.74 (11)
C3—C4—C5	117.90 (10)	F4—C10—C9	119.96 (11)
C4—C5—H5A	109.5	F4—C10—C11	120.23 (12)
C4—C5—H5B	109.5	C9—C10—C11	119.80 (12)
H5A—C5—H5B	109.5	F5—C11—C10	118.76 (11)
C4—C5—H5C	109.5	F5—C11—C6	119.36 (11)
H5A—C5—H5C	109.5	C10—C11—C6	121.87 (12)

C2 ⁱ —C1—C2—C3	-2.2 (3)	F1—C7—C8—C9	-179.14 (11)
C3 ⁱ —N1—C3—C2	3.3 (2)	C6—C7—C8—C9	-0.40 (19)
C3 ⁱ —N1—C3—C4	-174.53 (9)	F2—C8—C9—F3	1.46 (19)
C1—C2—C3—N1	-0.6 (2)	C7—C8—C9—F3	-178.34 (11)
C1—C2—C3—C4	177.14 (13)	F2—C8—C9—C10	-178.96 (11)
C6—N2—C4—C3	-179.98 (11)	C7—C8—C9—C10	1.24 (19)
C6—N2—C4—C5	-2.7 (2)	F3—C9—C10—F4	-0.11 (18)
N1—C3—C4—N2	164.92 (13)	C8—C9—C10—F4	-179.69 (11)
C2—C3—C4—N2	-12.97 (18)	F3—C9—C10—C11	179.21 (11)
N1—C3—C4—C5	-12.59 (17)	C8—C9—C10—C11	-0.38 (19)
C2—C3—C4—C5	169.52 (12)	F4—C10—C11—F5	-0.92 (18)
C4—N2—C6—C7	-62.67 (17)	C9—C10—C11—F5	179.76 (11)
C4—N2—C6—C11	123.67 (13)	F4—C10—C11—C6	177.94 (11)
C11—C6—C7—F1	177.46 (10)	C9—C10—C11—C6	-1.38 (19)
N2—C6—C7—F1	3.67 (18)	C7—C6—C11—F5	-178.99 (11)
C11—C6—C7—C8	-1.27 (18)	N2—C6—C11—F5	-4.89 (17)
N2—C6—C7—C8	-175.06 (11)	C7—C6—C11—C10	2.15 (18)
F1—C7—C8—F2	1.06 (18)	N2—C6—C11—C10	176.25 (11)
C6—C7—C8—F2	179.80 (11)		

Symmetry code: (i) $x, -y+1/2, z$.