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# Crystal structure of *fac*-{5-[(hexylazaniumyl)methyl]-2-(pyridin-2-yl)phenyl-$\kappa^2N,C^1$}bis[2-(pyridin-2-yl)phenyl-$\kappa^2N,C^1$]iridium(III) chloride

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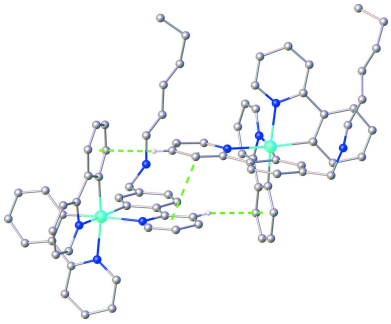
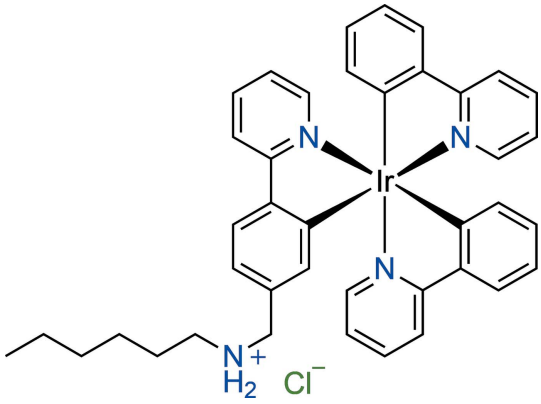
The asymmetric unit of the title compound, *fac*-[Ir($C_{11}H_8N$)$_2$($C_{18}H_{24}N_2$)]Cl or *fac*-[Ir(ppy)$_2$(Hppy-NC$_6$)]Cl, contains two [Ir(ppy)$_2$(ppy-NC$_6$)](H$^+$) cations, two Cl$^-$ anions and disordered solvent. In each complex molecule, the Ir$^{III}$ ion is coordinated by two *C*,*N*-bidentate 2-(pyridin-2-yl)phenyl ligands and one *C*,*N*-bidentate *N*-[4-(pyridin-2-yl)benzyl]hexan-1-aminium ligand, leading to a distorted *fac*-octahedral coordination environment. In the crystal, the molecules are linked by N—H$\cdots$Cl, C—H$\cdots\pi$ and $\pi$–$\pi$ interactions, forming a three-dimensional supramolecular structure. The hexyl group of one molecule is disordered over two orientations with a refined occupancy ratio of 0.412 (13):0.588 (13). The acetone and hexane solvent molecules were found to be highly disordered and their contribution to the scattering was masked using the solvent-masking routine smtbx.mask in *OLEX2* [Rees *et al.* (2005). *Acta Cryst.* D**61**, 1299–1301]. These solvent molecules are not considered in the given chemical formula and other crystal data.

## 1. Chemical context

Luminescent iridium complexes have attracted a significant amount of interest over the past decades as they have been shown to possess potential for use in a number of applications such as in organic-light emitting devices (OLED), cellular imaging and photoredox catalysis (You, 2013; You & Nam, 2012; König, 2017; Caporale & Massi, 2018). The beneficial photophysical properties of these complexes, which are at the core of their potential utilization, arise both from the properties of the Ir$^{3+}$ ion and its coordination environment. The large spin–orbit coupling constant of iridium ensures efficient involvement of triplet excited states in the photophysical properties, which results in luminescent lifetimes in the microsecond regime (Ladouceur, S. & Zysman-Colman, 2013; Zanoni *et al.*, 2015; Thorp-Greenwood *et al.*, 2012). This is significantly longer than for fluorescence from organic fluorophores, a benefit for imaging applications, yet also much shorter than phosphorescence lifetimes of organic phosphors, which is important for OLED applications. The NC cyclometalating ligands such as 2-phenylpyridine usually used to chelate the iridium center provide strong ligand fields, which result in lifting of the unfilled metal-based orbitals above the $\pi^*$ orbitals of the ligands, thus eliminating metal-centered



transitions from the photophysical properties (You & Nam, 2012). Thus, the usual electronic transitions present in the photochemistry of luminescent iridium complexes have charge–transfer characteristics such as metal-to-ligand charge transfer (MLCT) or ligand-to-ligand charger transfer (LLCT).




Luminescent iridium complexes can be divided into several distinct classes, one of which is tris-cyclometalated complexes. These complexes contain three cyclometalating NC ligands such 2-phenylpyridine (ppy) and the prototypical example of this structural class is [Ir(ppy)$_3$] (You & Nam, 2012). These complexes usually exhibit good photophysical properties. However, their use in cellular imaging is limited as they do not seem to be very readily taken up by cells (Fernández-Moreira *et al.*, 2010; Steunenberg *et al.*, 2012; Ho *et al.*, 2012). It has been noted that this problem can be alleviated by introducing protonatable groups into their structures, which helps them to become positively charged and thus be better taken up by cells (Kando *et al.*, 2015). We have recently reported two simple derivatives of the prototypical structure mentioned above, which contain an aminoalkyl side chain on one of the ppy ligands (Sansee *et al.*, 2016). The complexes differ only in the length of the alkyl chain, one being butyl while the other one is dodecyl. Both complexes are capable of staining live cells in fluorescence microscopy experiments. Furthermore, the complexes also exhibit ratiometric response to pH, which depends on their structure and is attributed to changes in their aggregation status. Several further analogues of these complexes are currently being investigated in order to obtain more detailed knowledge of the relationship between the structure of these compounds and their photophysical properties. The complex reported herein is one of these further compounds studied for this purpose.

## 2. Structural commentary

The asymmetric unit of the title compound contains two [Ir(ppy)$_2$(Hppy-NC$_6$)]$^+$ cations, two Cl$^-$ anions and disordered solvent molecules. In each complex molecule, the Ir$^{III}$ ion is coordinated by two *C*,*N*-bidentate ppy ligands and one *C*,*N*-bidentate Hppy-NC$_6$ ligand, leading to a distorted *fac*-octahedral coordination environment as shown in Fig. 1. The Ir—C and Ir—N bond lengths in the title compound range from 2.010 (6) to 2.036 (5) Å and 2.105 (5) to 2.144 (4) Å, respectively, whereas the bond angles in the [IrN$_3$C$_3$] octahedral core vary from 79.1 (2) to 172.1 (2)°. These structural features are typical of related iridium(III) complexes containing *C*,*N*-donor set ligands (Steunenberg *et al.*, 2012). The current molecule is isostructural with the butyl equivalent and displays similar packing and voids (see *Refinement* section) in the solid state. Full details of this structure have been published by Sansee *et al.* (2016).

## 3. Supramolecular features

In the crystal, pairs of cationic [Ir(ppy)$_2$(Hppy-NC$_6$)]$^+$ complex molecules are linked through N—H···Cl hydrogen bonds (Table 1) between the amino groups of the ppy-NC$_6$ ligands and chloride anions (Fig. 2) with an Ir···Ir separation

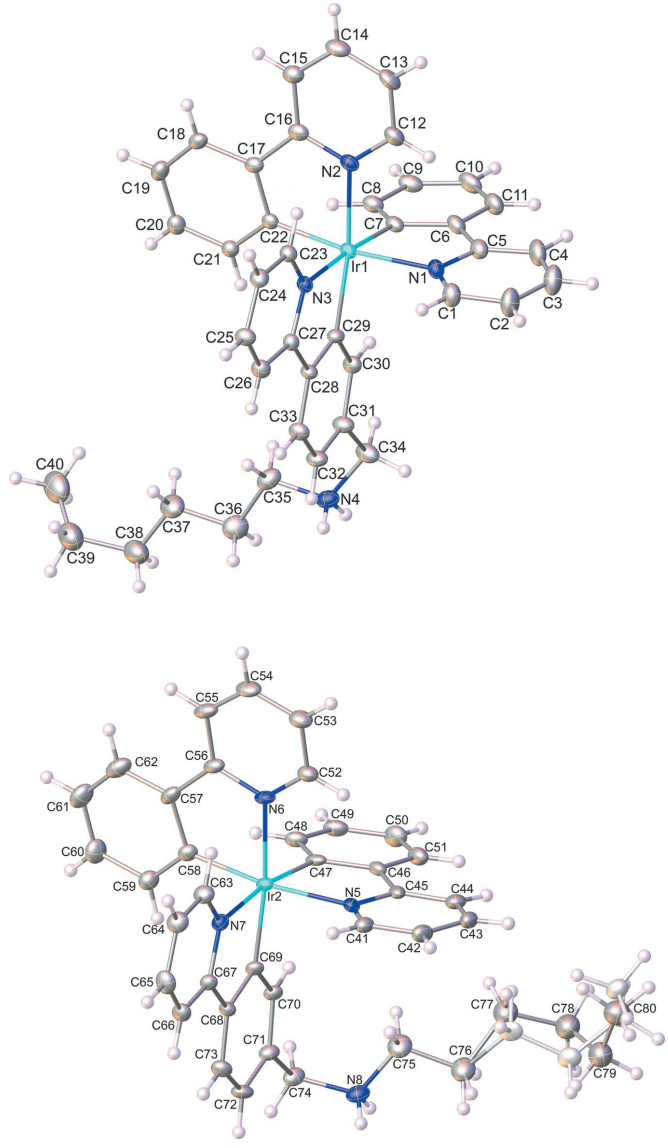



**Figure 1**
A view of the molecular structures of the two independent cationic molecules of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 35% probability level.

**Table 1**
Hydrogen-bond geometry (Å, °).

*Cg*1–*Cg*6 are the centroids of the C6–C11, N2/C12–C16, C17–C22, C46–C51, C57–C62 and C68–C73 rings, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N4—H4*A*···Cl2$^{i}$ | 0.89 | 2.30 | 3.172 (6) | 168 |
| N4—H4*B*···Cl1$^{i}$ | 0.89 | 2.26 | 3.142 (6) | 172 |
| N8—H8*A*···Cl2 | 0.89 | 2.21 | 3.073 (6) | 165 |
| N8—H8*B*···Cl1 | 0.89 | 2.16 | 3.044 (6) | 171 |
| C20—H20···*Cg*1$^{ii}$ | 0.93 | 3.12 | 3.497 (7) | 145 |
| C24—H24···*Cg*4$^{iii}$ | 0.93 | 2.89 | 3.532 (7) | 139 |
| C26—H26···*Cg*5 | 0.93 | 2.79 | 3.645 (7) | 158 |
| C34—H34*B*···*Cg*3$^{ii}$ | 0.97 | 2.91 | 3.422 (7) | 160 |
| C37—H37···*Cg*1$^{ii}$ | 0.97 | 3.01 | 3.818 (7) | 141 |
| C49—H49···*Cg*2$^{iii}$ | 0.93 | 3.07 | 3.705 (7) | 145 |
| C53—H53···*Cg*6$^{iii}$ | 0.93 | 3.10 | 3.692 (7) | 135 |
| C65—H65···*Cg*3 | 0.93 | 2.86 | 3.530 (7) | 135 |

Symmetry codes: (i) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+2, -y+1, -z+1$; (iii) $x, -y+\frac{1}{2}, z-\frac{3}{2}$.

of 15.8207 (7) Å. Simultaneously, pairs of cationic complexes with an Ir···Ir separation of 8.5468 (4) Å (Fig. 3) also interact with each other *via* a parallel fourfold phenyl embrace (Dance & Scudder, 1996), which contains one $\pi$–$\pi$ stacking [centroid-to-centroid distance between the N3/C23–C27 and N7/C63–C67 rings = 3.682 (3) Å; dihedral angle = 6.5 (5)°] and two edge-to-face (phenyl)-C—H···$\pi$(phenyl) interactions (H26···*Cg*5 = 2.79 Å and H65···*Cg*3 = 2.85 Å; *Cg*5 and *Cg*3 are the centroids of the C57–C62 and C17–C22 rings, respectively). Numerous weak (phenyl)-C—H···$\pi$(phenyl) and (methylene)-C—H···$\pi$(phenyl) are observed with H···centroid distances ranging from 2.79 to 3.12 Å (Table 1). In addition, a comparison of the effect of the alkyl chain length between the ppy-NC6 in the title compound and the related complex with ppy-NC4 (Sansee *et al.*, 2016) on the packing arrangement suggests that the key intermolecular interactions (N—H···Cl, C—H···$\pi$ and $\pi$–$\pi$) remain the same.

## 4. Photophysical properties

The photophysical properties of the title compound have also been investigated in dichloromethane solution and the results can be seen in Fig. 4, which shows normalized absorption and

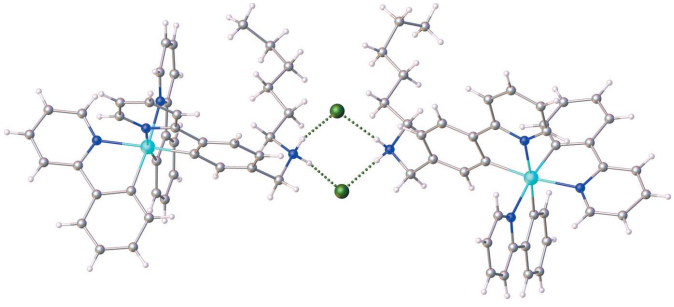


**Figure 2**
A perspective view of the title compound, showing the intermolecular N—H···Cl hydrogen bonds (dotted lines) between the two independent molecules.

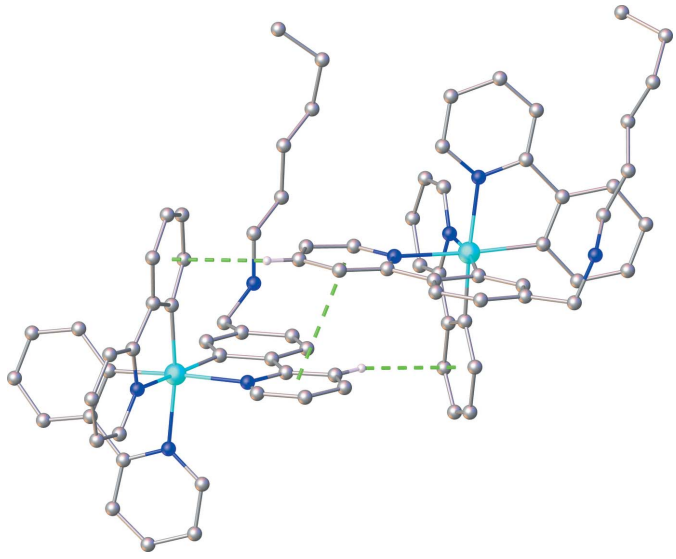


**Figure 3**
A perspective view showing the parallel fourfold phenyl embrace in the title compound.

emission spectra. The spectra exhibit the expected features, which are analogous to those of the parent complex and the complexes previously reported by our group. The absorption spectra can be roughly divided into three portions. The first portion lies between 250 and 320 nm and is mainly attributed to ligand-based $\pi$ to $\pi^*$ transitions. The second portion of this spectrum lies between 320 and 430 nm and is attributed to spin-allowed singlet metal-to-ligand charge transfer ($^1$MLCT) transition. Finally, the tail of the spectrum extending from 430 nm beyond 500 nm is attributed to spin-forbidden triplet metal-to-ligand charge transfer ($^3$MLCT). The emission spectrum exhibits a single unstructured peak centered at

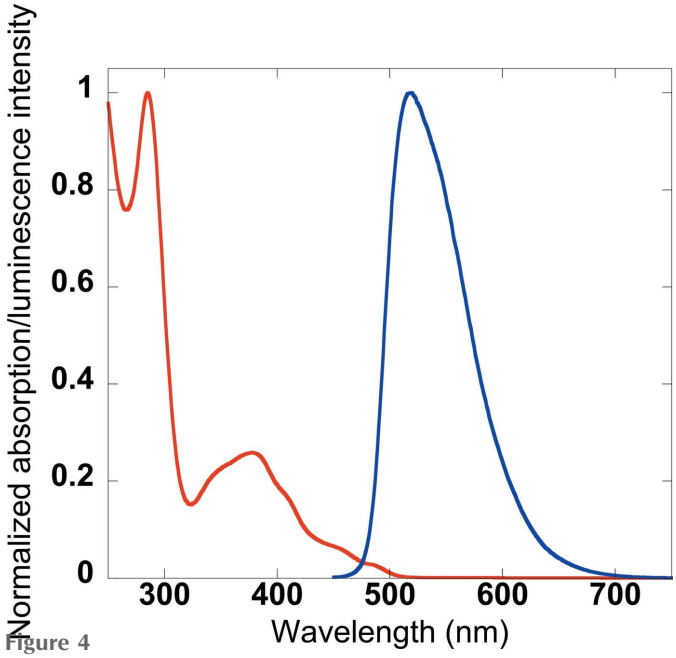



**Figure 4**
The photophysical properties of the title compound.

Table 2
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $[Ir(C_{11}H_8N)_2(C_{18}H_{24}N_2)]Cl$ |
| $M_r$ | 804.41 |
| Crystal system, space group | Monoclinic, $P2_1/c$ |
| Temperature (K) | 298 |
| $a, b, c$ (Å) | 12.1012 (7), 34.267 (2), 18.4681 (11) |
| $\beta$ (°) | 94.471 (2) |
| $V$ (Å$^3$) | 7634.9 (8) |
| $Z$ | 8 |
| Radiation type | Cu $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 7.64 |
| Crystal size (mm) | 0.18 × 0.1 × 0.1 |
| Data collection | |
| Diffractometer | Bruker D8 VENTURE |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2016) |
| $T_{min}$, $T_{max}$ | 0.635, 0.734 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 110242, 15577, 14944 |
| $R_{int}$ | 0.056 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.626 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.052, 0.135, 1.07 |
| No. of reflections | 15577 |
| No. of parameters | 869 |
| No. of restraints | 142 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 3.11, −1.29 |

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

520 nm. The photoluminescence quantum yield has been determined to be 39%.

## 5. Synthesis and crystallization

All chemicals and reagents were of commercial grade and were used without further purification. The complex *fac*-[Ir(ppy)$_2$(Fppy)] [ppy is 2-phenylpyridine and Fppy is 2-(2,4-difluorophenyl)pyridine] was prepared according to a literature procedure (Beeby *et al.*, 2003). $^1$H NMR spectra were recorded on a Bruker Advance 400MHz instrument operating at 400 MHz. The $^{13}$C NMR spectrum was recorded on the same instrument operating at 100 MHz for carbon. Mass spectra were acquired with an Agilent technologies UHD Accurate-Mass Q-TOF LC–MS instrument model 6540. UV-Visible absorption spectra were recorded using an Analytik Jena 210plus diode array spectrophotometer. Steady-state emission spectra were recorded using Fluoromax-4 and Fluorolog spectrofluorometers from Yvon Horiba. Phosphorescence lifetime measurements were performed on a DeltaFlexTM instrument equipped with a UV LED ($\lambda_{ex}$ = 372 nm).

*fac*-[Ir(ppy)$_3$(Fppy)] (200 mg, 0.29 mmol), *n*-hexylamine (90 µL, 0.44 mmol) and triethylamine (40 µL, 0.43 mmol) were suspended in a $CH_3OH/CH_2Cl_2$ (1:1) mixture (20 mL). The reaction mixture was heated to reflux for 10 h. The solution was left to cool to room temperature and $NaBH_4$ (37 mg, 0.58 mmol) was added. The reaction mixture was stirred at room temperature for 20 h. The solvent was removed under vacuum. The residue was dissolved in dichloromethane, dried over anhydrous sodium sulfate and filtered. The residue was purified by column chromatography on silica using gradient of methanol (up to 5%) in dichloromethane as the eluent. The pure product was isolated as an orange solid (yield 89.5%, 204 mg). Single crystals of the complex suitable for the single crystal X-ray diffraction analysis were grown by slow diffusion of hexane into its solution in acetone.

$^1$H NMR (400 MHz, DMSO-*d*6, $\delta$) 8.18 (*d*, *J* = 8.2 Hz, 1H), 8.13 (*d*, *J* = 8.0 Hz, 2H), 7.85–7.70 (*m*, 6H), 7.40–7.50 (*m*, 3H), 7.15–7.06 (*m*, 3H), 7.05 (*d*, *J* = 7.8 Hz, 1H), 6.75–6.85 (*m*, 2H), 6.70–6.65 (*m*, 5H), 3.67 (*s*, 2H), 2.52–2.65 (*m*, 2H), 1.47 (*m*, 2H), 1.32–1.21 (*m*, 6H), 0.85 (*t*, *J* = 6.7 Hz, 3H). $^{13}$C NMR (100 MHz, DMSO-*d*6, $\delta$) 165.5, 165.0, 161.2, 160.1, 146.8, 144.5, 143.7, 137.5, 137.0, 136.2, 133.0, 129.0, 124.2, 123.1, 122.8, 120.6, 119.7, 119.4, 119.1, 130.2, 130.0, 125.0, 124.1, 122.6, 122.4, 122.2, 122.1, 121.7, 120.4, 120.1, 119.3, 119.0, 118.8, 50.6, 46.1, 30.7, 25.8, 25.5, 21.9, 13.8. HRMS (ES$^+$) calculated for $C_{40}H_{40}IrN_4$ (769.2882); found 769.2937. In dichloromethane at 298 K, $\lambda_{ex}$ = 390 nm and $\lambda_{em}$ = 515 nm while the luminescence lifetime is 70 ns and 1.44 µs, respectively, for aerated and degassed solutions.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydrogen atoms attached to carbon atoms were placed in calculated positions and constrained to ride on their parent with $U_{iso}$(H) = 1.2$U_{eq}$(C) and a C—H distance of 0.93 Å for aromatic and 0.97 Å for methylene hydrogen atoms. The nitrogen-bound hydrogen atoms were located in a difference-Fourier map but were refined with a distance restraint of N—H = 0.89 Å with $U_{iso}$(H) = 1.2$U_{eq}$(N). The hexyl group of one complex is disordered over two orientations with a refined occupancy ratio of 0.412 (13):0.588 (13). Anisotropic displacement parameters of all atoms were restrained using enhanced rigid-bond restraints (RIGU command; Thorn *et al.*, 2012). All attempts to model disordered acetone or hexane as the solvents used for crystallization failed. Therefore, the solvent-masking routine smtbx.mask (Rees *et al.*, 2005) was used and found four solvent-accessible voids in the unit cell. Two of them are of 490 Å$^3$ in volume and contain an estimated 71 electrons; the other two are of 157 Å$^3$ in volume and contain an estimated 60 electrons. These electrons are attributable to four molecules of acetone and two molecules of hexane, which means that there are two molecules of acetone and one molecule of hexane per formula unit present in this structure.

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# supporting information

*Acta Cryst.* (2018). E**74**, 1439-1443 [https://doi.org/10.1107/S2056989018012811]

## Crystal structure of *fac*-{5-[(hexylazaniumyl)methyl]-2-(pyridin-2-yl)phenyl-$\kappa^2N,C^1$}bis[2-(pyridin-2-yl)phenyl-$\kappa^2N,C^1$]iridium(III) chloride

**Sureemas Meksawangwong, Suwadee Jiajaroen, Kittipong Chainok, Waraporn Pinyo and Filip Kielar**

### Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

### *fac*-{5-[(Hexylazaniumyl)methyl]-2-(pyridin-2-yl)phenyl-$\kappa^2N,C^1$}bis[2-(pyridin-2-yl)phenyl-$\kappa^2N,C^1$]iridium(III) chloride

*Crystal data*

$[Ir(C_{11}H_8N)_2(C_{18}H_{24}N_2)]Cl$
$M_r$ = 804.41
Monoclinic, $P2_1/c$
$a$ = 12.1012 (7) Å
$b$ = 34.267 (2) Å
$c$ = 18.4681 (11) Å
$\beta$ = 94.471 (2)°
$V$ = 7634.9 (8) Å$^3$
$Z$ = 8
$F(000)$ = 3216
$D_x$ = 1.400 Mg m$^{-3}$
Cu $K\alpha$ radiation, $\lambda$ = 1.54178 Å
Cell parameters from 9555 reflections
$\theta$ = 4.4–74.7°
$\mu$ = 7.64 mm$^{-1}$
$T$ = 298 K
Block, light yellow
0.18 × 0.1 × 0.1 mm

*Data collection*

Bruker D8 VENTURE diffractometer
Radiation source: X-ray tube, Micro focus tube
Graphite monochromator
Detector resolution: 10.4167 pixels mm$^{-1}$
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
$T_{min}$ = 0.635, $T_{max}$ = 0.734
110242 measured reflections
15577 independent reflections
14944 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.056
$\theta_{max}$ = 74.8°, $\theta_{min}$ = 4.5°
$h$ = −15→15
$k$ = −42→41
$l$ = −23→23

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.135
$S$ = 1.07
15577 reflections
869 parameters
142 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 49.4936P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 3.11$ e Å$^{-3}$
$\Delta\rho_{min} = -1.29$ e Å$^{-3}$

*Special details*

**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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Ir1 | 1.07478 (2) | 0.43998 (2) | 0.33055 (2) | 0.03495 (8) | |
| Ir2 | 0.76998 (2) | 0.24093 (2) | 0.51021 (2) | 0.03391 (8) | |
| Cl1 | 0.41899 (15) | 0.04389 (5) | 0.29918 (10) | 0.0557 (4) | |
| Cl2 | 0.28414 (15) | 0.17148 (5) | 0.23161 (11) | 0.0596 (5) | |
| N1 | 1.2374 (4) | 0.43256 (16) | 0.2959 (3) | 0.0437 (12) | |
| N2 | 1.0072 (5) | 0.45999 (14) | 0.2272 (3) | 0.0406 (11) | |
| N3 | 1.0194 (4) | 0.38123 (13) | 0.3108 (3) | 0.0342 (10) | |
| N4 | 1.2417 (5) | 0.41718 (18) | 0.6886 (3) | 0.0549 (15) | |
| H4A | 1.253977 | 0.391670 | 0.693468 | 0.066* | |
| H4B | 1.286575 | 0.429268 | 0.721868 | 0.066* | |
| N5 | 0.6118 (4) | 0.24667 (16) | 0.5517 (3) | 0.0377 (10) | |
| N6 | 0.8554 (5) | 0.26539 (15) | 0.6040 (3) | 0.0426 (12) | |
| N7 | 0.7597 (4) | 0.29451 (14) | 0.4543 (3) | 0.0374 (10) | |
| N8 | 0.4565 (5) | 0.12975 (17) | 0.3354 (3) | 0.0529 (14) | |
| H8A | 0.407718 | 0.145515 | 0.311668 | 0.064* | |
| H8B | 0.437654 | 0.105380 | 0.323207 | 0.064* | |
| C1 | 1.2805 (6) | 0.3999 (2) | 0.2736 (4) | 0.0588 (18) | |
| H1 | 1.238862 | 0.377185 | 0.275968 | 0.071* | |
| C2 | 1.3852 (7) | 0.3971 (3) | 0.2464 (6) | 0.078 (3) | |
| H2 | 1.412936 | 0.373439 | 0.230847 | 0.094* | |
| C3 | 1.4449 (8) | 0.4315 (3) | 0.2440 (6) | 0.084 (3) | |
| H3 | 1.515140 | 0.431231 | 0.226826 | 0.101* | |
| C4 | 1.4019 (7) | 0.4656 (3) | 0.2666 (5) | 0.071 (2) | |
| H4 | 1.441332 | 0.488668 | 0.262833 | 0.085* | |
| C5 | 1.2994 (6) | 0.4661 (2) | 0.2953 (4) | 0.0523 (16) | |
| C6 | 1.2458 (6) | 0.5001 (2) | 0.3268 (4) | 0.0486 (15) | |
| C7 | 1.1397 (5) | 0.49365 (17) | 0.3512 (3) | 0.0402 (13) | |
| C8 | 1.0913 (6) | 0.52524 (18) | 0.3849 (4) | 0.0467 (15) | |
| H8 | 1.022665 | 0.522019 | 0.403556 | 0.056* | |
| C9 | 1.1438 (7) | 0.56144 (19) | 0.3910 (4) | 0.0528 (17) | |
| H9 | 1.109226 | 0.581995 | 0.413173 | 0.063* | |
| C10 | 1.2451 (8) | 0.5672 (2) | 0.3650 (4) | 0.063 (2) | |
| H10 | 1.278324 | 0.591655 | 0.368465 | 0.076* | |
| C11 | 1.2982 (7) | 0.5366 (2) | 0.3334 (5) | 0.062 (2) | |
| H11 | 1.367952 | 0.540130 | 0.316615 | 0.074* | |
| C12 | 1.0618 (7) | 0.4635 (2) | 0.1662 (4) | 0.0530 (16) | |

| | | | | |
|---|---|---|---|---|
| H12 | 1.137046 | 0.457694 | 0.168323 | 0.064* |
| C13 | 1.0090 (7) | 0.4755 (2) | 0.1009 (4) | 0.0581 (19) |
| H13 | 1.047858 | 0.477186 | 0.059557 | 0.070* |
| C14 | 0.8963 (7) | 0.4849 (2) | 0.0980 (4) | 0.060 (2) |
| H14 | 0.859585 | 0.493610 | 0.054856 | 0.072* |
| C15 | 0.8421 (6) | 0.4813 (2) | 0.1581 (4) | 0.0503 (16) |
| H15 | 0.766948 | 0.487193 | 0.156224 | 0.060* |
| C16 | 0.8964 (6) | 0.46876 (17) | 0.2241 (4) | 0.0437 (14) |
| C17 | 0.8474 (5) | 0.46419 (16) | 0.2925 (3) | 0.0394 (13) |
| C18 | 0.7338 (5) | 0.47131 (17) | 0.3000 (4) | 0.0449 (14) |
| H18 | 0.686257 | 0.476464 | 0.259134 | 0.054* |
| C19 | 0.6941 (6) | 0.47065 (19) | 0.3666 (4) | 0.0491 (16) |
| H19 | 0.619008 | 0.474812 | 0.371028 | 0.059* |
| C20 | 0.7654 (6) | 0.46373 (18) | 0.4289 (4) | 0.0466 (15) |
| H20 | 0.738553 | 0.464669 | 0.474737 | 0.056* |
| C21 | 0.8754 (5) | 0.45555 (16) | 0.4216 (3) | 0.0371 (12) |
| H21 | 0.921882 | 0.450794 | 0.463135 | 0.045* |
| C22 | 0.9199 (5) | 0.45412 (15) | 0.3538 (3) | 0.0335 (11) |
| C23 | 0.9639 (5) | 0.36784 (18) | 0.2508 (3) | 0.0393 (13) |
| H23 | 0.947662 | 0.385117 | 0.212643 | 0.047* |
| C24 | 0.9291 (5) | 0.3295 (2) | 0.2424 (3) | 0.0453 (14) |
| H24 | 0.892515 | 0.320940 | 0.199101 | 0.054* |
| C25 | 0.9501 (6) | 0.30434 (18) | 0.2999 (4) | 0.0450 (14) |
| H25 | 0.927257 | 0.278454 | 0.296228 | 0.054* |
| C26 | 1.0051 (6) | 0.31783 (18) | 0.3624 (4) | 0.0444 (14) |
| H26 | 1.019251 | 0.301026 | 0.401604 | 0.053* |
| C27 | 1.0402 (5) | 0.35680 (16) | 0.3680 (3) | 0.0354 (12) |
| C28 | 1.0981 (5) | 0.37445 (16) | 0.4324 (3) | 0.0350 (12) |
| C29 | 1.1200 (5) | 0.41497 (16) | 0.4284 (3) | 0.0339 (11) |
| C30 | 1.1738 (5) | 0.43178 (18) | 0.4908 (4) | 0.0439 (14) |
| H30 | 1.189190 | 0.458368 | 0.490710 | 0.053* |
| C31 | 1.2051 (6) | 0.4101 (2) | 0.5529 (4) | 0.0497 (16) |
| C32 | 1.1826 (6) | 0.3705 (2) | 0.5553 (4) | 0.0483 (15) |
| H32 | 1.204135 | 0.355877 | 0.596429 | 0.058* |
| C33 | 1.1271 (6) | 0.35296 (18) | 0.4950 (4) | 0.0460 (15) |
| H33 | 1.109168 | 0.326601 | 0.496539 | 0.055* |
| C34 | 1.2727 (7) | 0.4294 (2) | 0.6147 (4) | 0.062 (2) |
| H34A | 1.350352 | 0.423451 | 0.610741 | 0.075* |
| H34B | 1.263922 | 0.457484 | 0.610190 | 0.075* |
| C35 | 1.1267 (7) | 0.4251 (2) | 0.7043 (5) | 0.064 (2) |
| H35A | 1.076578 | 0.410421 | 0.670985 | 0.076* |
| H35B | 1.110752 | 0.452614 | 0.697266 | 0.076* |
| C36 | 1.1083 (8) | 0.4140 (3) | 0.7800 (5) | 0.073 (2) |
| H36A | 1.155344 | 0.429654 | 0.813559 | 0.088* |
| H36B | 1.127931 | 0.386775 | 0.787973 | 0.088* |
| C37 | 0.9843 (8) | 0.4204 (3) | 0.7947 (5) | 0.083 (3) |
| H37A | 0.966255 | 0.447789 | 0.788417 | 0.100* |
| H37B | 0.937763 | 0.405752 | 0.759177 | 0.100* |

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|---|---|---|---|---|
| C38 | 0.9596 (9) | 0.4083 (4) | 0.8668 (6) | 0.098 (4) |
| H38A | 0.998248 | 0.425613 | 0.901877 | 0.118* |
| H38B | 0.988682 | 0.382255 | 0.875582 | 0.118* |
| C39 | 0.8353 (10) | 0.4083 (4) | 0.8805 (8) | 0.112 (4) |
| H39A | 0.797533 | 0.390370 | 0.846225 | 0.134* |
| H39B | 0.828054 | 0.397945 | 0.928773 | 0.134* |
| C40 | 0.7766 (12) | 0.4461 (5) | 0.8747 (9) | 0.126 (5) |
| H40A | 0.787910 | 0.457969 | 0.828764 | 0.189* |
| H40B | 0.805067 | 0.463033 | 0.913256 | 0.189* |
| H40C | 0.698808 | 0.442000 | 0.878431 | 0.189* |
| C41 | 0.5498 (6) | 0.2789 (2) | 0.5490 (4) | 0.0499 (16) |
| H41 | 0.574054 | 0.300487 | 0.524073 | 0.060* |
| C42 | 0.4508 (6) | 0.2816 (3) | 0.5817 (4) | 0.0590 (19) |
| H42 | 0.408551 | 0.304268 | 0.578837 | 0.071* |
| C43 | 0.4169 (6) | 0.2486 (3) | 0.6194 (4) | 0.064 (2) |
| H43 | 0.352423 | 0.249338 | 0.643691 | 0.077* |
| C44 | 0.4783 (6) | 0.2158 (3) | 0.6202 (4) | 0.0558 (18) |
| H44 | 0.453430 | 0.193530 | 0.642478 | 0.067* |
| C45 | 0.5781 (5) | 0.2149 (2) | 0.5882 (3) | 0.0441 (15) |
| C46 | 0.6555 (5) | 0.18172 (19) | 0.5898 (3) | 0.0423 (14) |
| C47 | 0.7542 (5) | 0.18778 (17) | 0.5566 (3) | 0.0418 (14) |
| C48 | 0.8281 (6) | 0.15588 (18) | 0.5553 (4) | 0.0473 (15) |
| H48 | 0.894588 | 0.158848 | 0.533847 | 0.057* |
| C49 | 0.8031 (7) | 0.1205 (2) | 0.5853 (4) | 0.0555 (18) |
| H49 | 0.852789 | 0.099886 | 0.583297 | 0.067* |
| C50 | 0.7073 (7) | 0.1150 (2) | 0.6178 (5) | 0.064 (2) |
| H50 | 0.692256 | 0.090885 | 0.637860 | 0.076* |
| C51 | 0.6315 (7) | 0.1455 (3) | 0.6213 (4) | 0.063 (2) |
| H51 | 0.566181 | 0.141948 | 0.643890 | 0.076* |
| C52 | 0.8091 (6) | 0.2805 (2) | 0.6618 (4) | 0.0507 (16) |
| H52 | 0.733148 | 0.277643 | 0.664972 | 0.061* |
| C53 | 0.8708 (7) | 0.3000 (2) | 0.7166 (4) | 0.0605 (19) |
| H53 | 0.837146 | 0.310114 | 0.756032 | 0.073* |
| C54 | 0.9818 (7) | 0.3040 (2) | 0.7116 (4) | 0.066 (2) |
| H54 | 1.024160 | 0.317916 | 0.747001 | 0.079* |
| C55 | 1.0308 (6) | 0.2878 (2) | 0.6553 (4) | 0.057 (2) |
| H55 | 1.107096 | 0.289922 | 0.653051 | 0.068* |
| C56 | 0.9670 (5) | 0.26793 (18) | 0.6006 (4) | 0.0444 (15) |
| C57 | 1.0098 (5) | 0.24927 (19) | 0.5357 (4) | 0.0465 (15) |
| C58 | 0.9277 (5) | 0.23316 (17) | 0.4857 (4) | 0.0409 (13) |
| C59 | 0.9663 (6) | 0.2147 (2) | 0.4258 (4) | 0.0491 (15) |
| H59 | 0.915836 | 0.203917 | 0.390780 | 0.059* |
| C60 | 1.0815 (7) | 0.2119 (2) | 0.4170 (5) | 0.063 (2) |
| H60 | 1.105394 | 0.199287 | 0.376449 | 0.075* |
| C61 | 1.1573 (7) | 0.2274 (3) | 0.4669 (6) | 0.070 (2) |
| H61 | 1.232616 | 0.225364 | 0.460704 | 0.084* |
| C62 | 1.1224 (7) | 0.2460 (2) | 0.5260 (5) | 0.065 (2) |
| H62 | 1.174177 | 0.256581 | 0.560357 | 0.078* |

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|---|---|---|---|---|---|
| C63 | 0.7952 (6) | 0.32935 (19) | 0.4802 (4) | 0.0491 (15) | |
| H63 | 0.831443 | 0.330229 | 0.526458 | 0.059* | |
| C64 | 0.7811 (6) | 0.36363 (19) | 0.4425 (4) | 0.0530 (17) | |
| H64 | 0.805441 | 0.387149 | 0.463244 | 0.064* | |
| C65 | 0.7303 (7) | 0.3625 (2) | 0.3734 (4) | 0.0555 (18) | |
| H65 | 0.721146 | 0.385217 | 0.346211 | 0.067* | |
| C66 | 0.6933 (5) | 0.32747 (19) | 0.3450 (4) | 0.0455 (14) | |
| H66 | 0.657922 | 0.326505 | 0.298429 | 0.055* | |
| C67 | 0.7084 (5) | 0.29345 (17) | 0.3854 (3) | 0.0368 (12) | |
| C68 | 0.6741 (5) | 0.25362 (17) | 0.3615 (3) | 0.0343 (11) | |
| C69 | 0.6989 (5) | 0.22348 (17) | 0.4136 (3) | 0.0356 (12) | |
| C70 | 0.6660 (5) | 0.18595 (17) | 0.3923 (3) | 0.0375 (12) | |
| H70 | 0.684364 | 0.165287 | 0.423547 | 0.045* | |
| C71 | 0.6078 (5) | 0.17814 (18) | 0.3272 (4) | 0.0423 (13) | |
| C72 | 0.5840 (6) | 0.2087 (2) | 0.2768 (4) | 0.0494 (16) | |
| H72 | 0.545540 | 0.203752 | 0.232143 | 0.059* | |
| C73 | 0.6187 (6) | 0.24592 (19) | 0.2951 (4) | 0.0462 (15) | |
| H73 | 0.604543 | 0.266161 | 0.262121 | 0.055* | |
| C74 | 0.5677 (6) | 0.1377 (2) | 0.3095 (4) | 0.0498 (16) | |
| H74A | 0.564341 | 0.134023 | 0.257347 | 0.060* | |
| H74B | 0.620452 | 0.119107 | 0.331592 | 0.060* | |
| C75 | 0.4457 (7) | 0.1345 (3) | 0.4145 (5) | 0.067 (2) | |
| H75A | 0.459328 | 0.161505 | 0.428261 | 0.081* | |
| H75B | 0.500241 | 0.118398 | 0.441611 | 0.081* | |
| C76 | 0.3303 (9) | 0.1228 (3) | 0.4325 (5) | 0.083 (3) | |
| H76A | 0.324515 | 0.094587 | 0.428812 | 0.100* | 0.412 (13) |
| H76B | 0.277466 | 0.133770 | 0.395918 | 0.100* | 0.412 (13) |
| H76C | 0.306827 | 0.099206 | 0.406568 | 0.100* | 0.588 (13) |
| H76D | 0.277521 | 0.143371 | 0.419445 | 0.100* | 0.588 (13) |
| C77 | 0.2953 (14) | 0.1351 (5) | 0.5082 (8) | 0.054 (3) | 0.412 (13) |
| H77A | 0.347486 | 0.124352 | 0.545518 | 0.065* | 0.412 (13) |
| H77B | 0.297884 | 0.163272 | 0.512146 | 0.065* | 0.412 (13) |
| C77A | 0.3386 (16) | 0.1154 (7) | 0.5185 (8) | 0.090 (4) | 0.588 (13) |
| H77C | 0.405021 | 0.100376 | 0.532153 | 0.108* | 0.588 (13) |
| H77D | 0.345233 | 0.140260 | 0.543466 | 0.108* | 0.588 (13) |
| C78 | 0.1840 (16) | 0.1215 (7) | 0.5202 (10) | 0.067 (3) | 0.412 (13) |
| H78A | 0.177213 | 0.094476 | 0.505158 | 0.080* | 0.412 (13) |
| H78B | 0.131041 | 0.136550 | 0.489450 | 0.080* | 0.412 (13) |
| C78A | 0.2409 (14) | 0.0942 (6) | 0.5424 (13) | 0.102 (4) | 0.588 (13) |
| H78C | 0.259008 | 0.083001 | 0.590117 | 0.122* | 0.588 (13) |
| H78D | 0.221646 | 0.072989 | 0.508917 | 0.122* | 0.588 (13) |
| C79 | 0.1531 (18) | 0.1248 (6) | 0.5994 (11) | 0.067 (3) | 0.412 (13) |
| H79A | 0.076702 | 0.116498 | 0.601059 | 0.080* | 0.412 (13) |
| H79B | 0.198849 | 0.106574 | 0.628620 | 0.080* | 0.412 (13) |
| C79A | 0.1412 (16) | 0.1218 (6) | 0.5454 (12) | 0.099 (3) | 0.588 (13) |
| H79C | 0.131299 | 0.135653 | 0.499502 | 0.119* | 0.588 (13) |
| H79D | 0.075296 | 0.106112 | 0.549784 | 0.119* | 0.588 (13) |
| C80 | 0.1650 (19) | 0.1640 (6) | 0.6337 (14) | 0.068 (4) | 0.412 (13) |

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|---|---|---|---|---|---|
| H80A | 0.106664 | 0.180731 | 0.613881 | 0.102* | 0.412 (13) |
| H80B | 0.235434 | 0.174945 | 0.624230 | 0.102* | 0.412 (13) |
| H80C | 0.160575 | 0.161567 | 0.685198 | 0.102* | 0.412 (13) |
| C80A | 0.149 (2) | 0.1505 (7) | 0.6040 (12) | 0.102 (4) | 0.588 (13) |
| H80D | 0.092408 | 0.170046 | 0.594490 | 0.153* | 0.588 (13) |
| H80E | 0.220302 | 0.162577 | 0.606797 | 0.153* | 0.588 (13) |
| H80F | 0.137666 | 0.137751 | 0.649155 | 0.153* | 0.588 (13) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ir1 | 0.03986 (14) | 0.03253 (13) | 0.03194 (13) | −0.00881 (9) | −0.00058 (10) | 0.00123 (9) |
| Ir2 | 0.03531 (13) | 0.03230 (13) | 0.03245 (13) | −0.00578 (9) | −0.00788 (9) | 0.00281 (9) |
| Cl1 | 0.0552 (9) | 0.0412 (8) | 0.0675 (11) | 0.0030 (7) | −0.0152 (8) | −0.0086 (7) |
| Cl2 | 0.0564 (9) | 0.0473 (8) | 0.0701 (11) | −0.0028 (7) | −0.0264 (8) | 0.0008 (8) |
| N1 | 0.041 (3) | 0.052 (3) | 0.039 (3) | −0.011 (2) | 0.005 (2) | −0.001 (2) |
| N2 | 0.054 (3) | 0.034 (2) | 0.033 (3) | −0.011 (2) | −0.001 (2) | 0.003 (2) |
| N3 | 0.037 (2) | 0.032 (2) | 0.033 (2) | −0.0083 (19) | 0.0011 (19) | −0.0016 (19) |
| N4 | 0.061 (4) | 0.048 (3) | 0.052 (3) | −0.002 (3) | −0.017 (3) | 0.001 (3) |
| N5 | 0.036 (2) | 0.051 (3) | 0.026 (2) | −0.002 (2) | −0.0002 (19) | 0.000 (2) |
| N6 | 0.048 (3) | 0.042 (3) | 0.035 (3) | −0.012 (2) | −0.016 (2) | 0.001 (2) |
| N7 | 0.035 (2) | 0.035 (2) | 0.041 (3) | −0.0025 (19) | 0.000 (2) | 0.000 (2) |
| N8 | 0.054 (3) | 0.044 (3) | 0.058 (4) | −0.004 (2) | −0.015 (3) | −0.008 (3) |
| C1 | 0.051 (4) | 0.062 (4) | 0.064 (5) | −0.014 (3) | 0.009 (3) | −0.008 (4) |
| C2 | 0.055 (5) | 0.090 (7) | 0.093 (7) | −0.007 (4) | 0.024 (5) | −0.018 (5) |
| C3 | 0.055 (5) | 0.103 (8) | 0.096 (7) | −0.020 (5) | 0.019 (5) | −0.020 (6) |
| C4 | 0.054 (4) | 0.089 (6) | 0.070 (5) | −0.030 (4) | 0.011 (4) | −0.003 (5) |
| C5 | 0.047 (4) | 0.059 (4) | 0.050 (4) | −0.017 (3) | −0.002 (3) | 0.005 (3) |
| C6 | 0.057 (4) | 0.051 (4) | 0.038 (3) | −0.020 (3) | 0.002 (3) | 0.005 (3) |
| C7 | 0.049 (3) | 0.037 (3) | 0.033 (3) | −0.014 (3) | −0.005 (2) | 0.004 (2) |
| C8 | 0.062 (4) | 0.038 (3) | 0.039 (3) | −0.009 (3) | −0.005 (3) | 0.003 (3) |
| C9 | 0.081 (5) | 0.038 (3) | 0.036 (3) | −0.008 (3) | −0.009 (3) | −0.001 (3) |
| C10 | 0.086 (6) | 0.047 (4) | 0.056 (4) | −0.030 (4) | −0.002 (4) | 0.008 (3) |
| C11 | 0.060 (4) | 0.061 (5) | 0.063 (5) | −0.025 (4) | 0.002 (4) | 0.010 (4) |
| C12 | 0.065 (4) | 0.047 (4) | 0.049 (4) | −0.008 (3) | 0.009 (3) | 0.008 (3) |
| C13 | 0.078 (5) | 0.058 (4) | 0.040 (4) | −0.009 (4) | 0.018 (3) | 0.008 (3) |
| C14 | 0.087 (6) | 0.051 (4) | 0.039 (4) | −0.010 (4) | −0.013 (4) | 0.007 (3) |
| C15 | 0.059 (4) | 0.043 (3) | 0.047 (4) | −0.006 (3) | −0.007 (3) | 0.003 (3) |
| C16 | 0.057 (4) | 0.028 (3) | 0.044 (3) | −0.009 (3) | −0.007 (3) | 0.001 (2) |
| C17 | 0.046 (3) | 0.028 (3) | 0.043 (3) | −0.007 (2) | −0.008 (3) | 0.002 (2) |
| C18 | 0.043 (3) | 0.032 (3) | 0.058 (4) | −0.002 (2) | −0.009 (3) | 0.007 (3) |
| C19 | 0.040 (3) | 0.038 (3) | 0.068 (5) | 0.000 (3) | 0.000 (3) | 0.000 (3) |
| C20 | 0.050 (4) | 0.034 (3) | 0.056 (4) | −0.002 (3) | 0.007 (3) | −0.003 (3) |
| C21 | 0.041 (3) | 0.031 (3) | 0.039 (3) | −0.005 (2) | −0.002 (2) | −0.001 (2) |
| C22 | 0.039 (3) | 0.023 (2) | 0.038 (3) | −0.007 (2) | −0.002 (2) | 0.000 (2) |
| C23 | 0.042 (3) | 0.040 (3) | 0.036 (3) | −0.007 (2) | 0.001 (2) | 0.000 (2) |
| C24 | 0.048 (3) | 0.050 (4) | 0.037 (3) | −0.009 (3) | −0.004 (3) | −0.006 (3) |
| C25 | 0.058 (4) | 0.034 (3) | 0.042 (3) | −0.007 (3) | −0.006 (3) | −0.002 (2) |

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|---|---|---|---|---|---|---|
| C26 | 0.052 (4) | 0.034 (3) | 0.047 (4) | −0.004 (3) | 0.001 (3) | −0.002 (3) |
| C27 | 0.036 (3) | 0.033 (3) | 0.037 (3) | −0.006 (2) | 0.002 (2) | −0.002 (2) |
| C28 | 0.040 (3) | 0.035 (3) | 0.029 (3) | −0.005 (2) | −0.003 (2) | 0.004 (2) |
| C29 | 0.039 (3) | 0.034 (3) | 0.027 (3) | 0.000 (2) | −0.004 (2) | 0.003 (2) |
| C30 | 0.047 (3) | 0.035 (3) | 0.049 (4) | −0.011 (3) | −0.005 (3) | 0.002 (3) |
| C31 | 0.061 (4) | 0.045 (3) | 0.040 (3) | −0.011 (3) | −0.014 (3) | 0.005 (3) |
| C32 | 0.058 (4) | 0.045 (3) | 0.039 (3) | −0.006 (3) | −0.013 (3) | 0.004 (3) |
| C33 | 0.060 (4) | 0.032 (3) | 0.045 (3) | −0.009 (3) | −0.003 (3) | 0.002 (3) |
| C34 | 0.078 (5) | 0.056 (4) | 0.050 (4) | −0.025 (4) | −0.014 (4) | 0.006 (3) |
| C35 | 0.060 (5) | 0.060 (5) | 0.068 (5) | 0.004 (4) | −0.017 (4) | −0.013 (4) |
| C36 | 0.083 (6) | 0.066 (5) | 0.069 (6) | −0.002 (4) | −0.003 (5) | −0.017 (4) |
| C37 | 0.075 (6) | 0.099 (7) | 0.072 (6) | −0.024 (5) | −0.019 (5) | 0.008 (5) |
| C38 | 0.088 (7) | 0.106 (8) | 0.097 (8) | −0.027 (6) | −0.011 (6) | 0.029 (7) |
| C39 | 0.099 (9) | 0.126 (11) | 0.109 (10) | −0.030 (8) | 0.005 (7) | 0.023 (8) |
| C40 | 0.107 (10) | 0.143 (13) | 0.125 (11) | −0.061 (10) | −0.010 (8) | 0.011 (10) |
| C41 | 0.042 (3) | 0.068 (4) | 0.039 (3) | −0.003 (3) | −0.005 (3) | −0.005 (3) |
| C42 | 0.041 (4) | 0.088 (6) | 0.047 (4) | 0.012 (4) | −0.002 (3) | −0.005 (4) |
| C43 | 0.038 (4) | 0.114 (7) | 0.039 (4) | −0.010 (4) | 0.000 (3) | 0.000 (4) |
| C44 | 0.044 (4) | 0.082 (5) | 0.039 (3) | −0.008 (4) | −0.010 (3) | 0.002 (3) |
| C45 | 0.040 (3) | 0.067 (4) | 0.025 (3) | −0.019 (3) | −0.006 (2) | 0.003 (3) |
| C46 | 0.049 (3) | 0.049 (3) | 0.027 (3) | −0.016 (3) | −0.007 (2) | 0.009 (2) |
| C47 | 0.050 (3) | 0.039 (3) | 0.033 (3) | −0.017 (3) | −0.021 (3) | 0.009 (2) |
| C48 | 0.058 (4) | 0.038 (3) | 0.043 (3) | −0.002 (3) | −0.015 (3) | 0.007 (3) |
| C49 | 0.070 (5) | 0.044 (4) | 0.049 (4) | −0.001 (3) | −0.020 (3) | 0.008 (3) |
| C50 | 0.073 (5) | 0.051 (4) | 0.065 (5) | −0.010 (4) | −0.005 (4) | 0.023 (4) |
| C51 | 0.066 (5) | 0.077 (5) | 0.046 (4) | −0.027 (4) | −0.007 (3) | 0.018 (4) |
| C52 | 0.058 (4) | 0.054 (4) | 0.038 (3) | −0.011 (3) | −0.008 (3) | 0.003 (3) |
| C53 | 0.073 (5) | 0.061 (4) | 0.045 (4) | −0.013 (4) | −0.010 (4) | −0.005 (3) |
| C54 | 0.078 (5) | 0.064 (5) | 0.050 (4) | −0.032 (4) | −0.024 (4) | 0.001 (4) |
| C55 | 0.058 (4) | 0.053 (4) | 0.054 (4) | −0.021 (3) | −0.026 (3) | 0.015 (3) |
| C56 | 0.047 (3) | 0.039 (3) | 0.044 (3) | −0.013 (3) | −0.016 (3) | 0.009 (3) |
| C57 | 0.033 (3) | 0.042 (3) | 0.062 (4) | −0.004 (2) | −0.011 (3) | 0.017 (3) |
| C58 | 0.040 (3) | 0.035 (3) | 0.046 (3) | 0.001 (2) | −0.006 (3) | 0.007 (3) |
| C59 | 0.045 (3) | 0.044 (3) | 0.058 (4) | 0.001 (3) | −0.001 (3) | 0.001 (3) |
| C60 | 0.053 (4) | 0.060 (4) | 0.077 (5) | 0.014 (3) | 0.015 (4) | 0.002 (4) |
| C61 | 0.044 (4) | 0.062 (5) | 0.102 (7) | 0.007 (4) | −0.002 (4) | 0.013 (5) |
| C62 | 0.050 (4) | 0.052 (4) | 0.089 (6) | −0.006 (3) | −0.021 (4) | 0.015 (4) |
| C63 | 0.055 (4) | 0.041 (3) | 0.050 (4) | −0.011 (3) | −0.004 (3) | −0.001 (3) |
| C64 | 0.060 (4) | 0.035 (3) | 0.063 (4) | −0.005 (3) | 0.000 (3) | 0.000 (3) |
| C65 | 0.069 (5) | 0.036 (3) | 0.063 (5) | 0.002 (3) | 0.014 (4) | 0.016 (3) |
| C66 | 0.047 (3) | 0.042 (3) | 0.046 (3) | −0.001 (3) | −0.001 (3) | 0.012 (3) |
| C67 | 0.036 (3) | 0.036 (3) | 0.038 (3) | 0.000 (2) | −0.003 (2) | 0.005 (2) |
| C68 | 0.037 (3) | 0.037 (3) | 0.027 (3) | −0.001 (2) | −0.001 (2) | 0.004 (2) |
| C69 | 0.034 (3) | 0.036 (3) | 0.035 (3) | 0.001 (2) | −0.009 (2) | 0.007 (2) |
| C70 | 0.036 (3) | 0.035 (3) | 0.040 (3) | 0.001 (2) | −0.009 (2) | 0.003 (2) |
| C71 | 0.041 (3) | 0.040 (3) | 0.044 (3) | −0.002 (2) | −0.008 (3) | −0.008 (3) |
| C72 | 0.052 (4) | 0.058 (4) | 0.036 (3) | 0.001 (3) | −0.016 (3) | −0.001 (3) |
| C73 | 0.053 (4) | 0.045 (3) | 0.040 (3) | 0.006 (3) | −0.007 (3) | 0.008 (3) |

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|---|---|---|---|---|---|---|
| C74 | 0.047 (4) | 0.047 (4) | 0.054 (4) | 0.001 (3) | −0.004 (3) | −0.015 (3) |
| C75 | 0.074 (5) | 0.063 (5) | 0.062 (5) | −0.021 (4) | −0.007 (4) | −0.014 (4) |
| C76 | 0.082 (6) | 0.085 (6) | 0.083 (6) | −0.033 (5) | 0.005 (5) | −0.019 (5) |
| C77 | 0.061 (4) | 0.036 (7) | 0.066 (5) | 0.016 (4) | 0.000 (4) | 0.023 (5) |
| C77A | 0.089 (4) | 0.110 (7) | 0.071 (9) | −0.010 (4) | 0.009 (5) | −0.012 (7) |
| C78 | 0.065 (4) | 0.066 (6) | 0.069 (4) | 0.005 (5) | 0.002 (4) | 0.020 (4) |
| C78A | 0.087 (4) | 0.117 (6) | 0.103 (9) | −0.005 (4) | 0.011 (5) | 0.009 (5) |
| C79 | 0.062 (6) | 0.069 (5) | 0.069 (4) | 0.002 (5) | 0.001 (4) | 0.018 (4) |
| C79A | 0.092 (4) | 0.122 (6) | 0.085 (7) | 0.001 (4) | 0.017 (5) | 0.018 (5) |
| C80 | 0.062 (11) | 0.070 (5) | 0.072 (5) | −0.001 (5) | 0.006 (6) | 0.016 (4) |
| C80A | 0.105 (9) | 0.119 (7) | 0.082 (7) | 0.011 (7) | 0.007 (6) | 0.021 (5) |

*Geometric parameters (Å, º)*

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|---|---|---|---|
| Ir1—N1 | 2.132 (5) | C38—H38B | 0.9700 |
| Ir1—N2 | 2.131 (5) | C38—C39 | 1.544 (14) |
| Ir1—N3 | 2.144 (4) | C39—H39A | 0.9700 |
| Ir1—C7 | 2.024 (6) | C39—H39B | 0.9700 |
| Ir1—C22 | 2.015 (6) | C39—C40 | 1.478 (19) |
| Ir1—C29 | 2.036 (5) | C40—H40A | 0.9600 |
| Ir2—N5 | 2.125 (5) | C40—H40B | 0.9600 |
| Ir2—N6 | 2.119 (5) | C40—H40C | 0.9600 |
| Ir2—N7 | 2.105 (5) | C41—H41 | 0.9300 |
| Ir2—C47 | 2.028 (6) | C41—C42 | 1.387 (10) |
| Ir2—C58 | 2.013 (6) | C42—H42 | 0.9300 |
| Ir2—C69 | 2.010 (6) | C42—C43 | 1.407 (12) |
| N1—C1 | 1.315 (10) | C43—H43 | 0.9300 |
| N1—C5 | 1.373 (8) | C43—C44 | 1.344 (12) |
| N2—C12 | 1.354 (9) | C44—H44 | 0.9300 |
| N2—C16 | 1.371 (9) | C44—C45 | 1.384 (10) |
| N3—C23 | 1.332 (7) | C45—C46 | 1.471 (10) |
| N3—C27 | 1.355 (7) | C46—C47 | 1.399 (9) |
| N4—H4A | 0.8900 | C46—C51 | 1.412 (10) |
| N4—H4B | 0.8900 | C47—C48 | 1.414 (10) |
| N4—C34 | 1.503 (10) | C48—H48 | 0.9300 |
| N4—C35 | 1.469 (10) | C48—C49 | 1.377 (9) |
| N5—C41 | 1.334 (9) | C49—H49 | 0.9300 |
| N5—C45 | 1.362 (8) | C49—C50 | 1.360 (12) |
| N6—C52 | 1.347 (9) | C50—H50 | 0.9300 |
| N6—C56 | 1.359 (9) | C50—C51 | 1.394 (13) |
| N7—C63 | 1.344 (8) | C51—H51 | 0.9300 |
| N7—C67 | 1.372 (8) | C52—H52 | 0.9300 |
| N8—H8A | 0.8900 | C52—C53 | 1.382 (10) |
| N8—H8B | 0.8900 | C53—H53 | 0.9300 |
| N8—C74 | 1.488 (9) | C53—C54 | 1.360 (12) |
| N8—C75 | 1.485 (10) | C54—H54 | 0.9300 |
| C1—H1 | 0.9300 | C54—C55 | 1.355 (13) |
| C1—C2 | 1.402 (11) | C55—H55 | 0.9300 |

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|---|---|---|---|
| C2—H2 | 0.9300 | C55—C56 | 1.401 (9) |
| C2—C3 | 1.386 (14) | C56—C57 | 1.486 (11) |
| C3—H3 | 0.9300 | C57—C58 | 1.414 (9) |
| C3—C4 | 1.358 (14) | C57—C62 | 1.393 (11) |
| C4—H4 | 0.9300 | C58—C59 | 1.388 (10) |
| C4—C5 | 1.386 (11) | C59—H59 | 0.9300 |
| C5—C6 | 1.473 (11) | C59—C60 | 1.419 (10) |
| C6—C7 | 1.411 (9) | C60—H60 | 0.9300 |
| C6—C11 | 1.403 (10) | C60—C61 | 1.357 (13) |
| C7—C8 | 1.399 (10) | C61—H61 | 0.9300 |
| C8—H8 | 0.9300 | C61—C62 | 1.359 (14) |
| C8—C9 | 1.394 (9) | C62—H62 | 0.9300 |
| C9—H9 | 0.9300 | C63—H63 | 0.9300 |
| C9—C10 | 1.366 (12) | C63—C64 | 1.369 (10) |
| C10—H10 | 0.9300 | C64—H64 | 0.9300 |
| C10—C11 | 1.383 (13) | C64—C65 | 1.373 (11) |
| C11—H11 | 0.9300 | C65—H65 | 0.9300 |
| C12—H12 | 0.9300 | C65—C66 | 1.371 (10) |
| C12—C13 | 1.381 (11) | C66—H66 | 0.9300 |
| C13—H13 | 0.9300 | C66—C67 | 1.389 (8) |
| C13—C14 | 1.398 (12) | C67—C68 | 1.483 (8) |
| C14—H14 | 0.9300 | C68—C69 | 1.428 (8) |
| C14—C15 | 1.340 (11) | C68—C73 | 1.377 (9) |
| C15—H15 | 0.9300 | C69—C70 | 1.394 (8) |
| C15—C16 | 1.406 (9) | C70—H70 | 0.9300 |
| C16—C17 | 1.445 (9) | C70—C71 | 1.371 (8) |
| C17—C18 | 1.413 (9) | C71—C72 | 1.416 (9) |
| C17—C22 | 1.419 (8) | C71—C74 | 1.495 (9) |
| C18—H18 | 0.9300 | C72—H72 | 0.9300 |
| C18—C19 | 1.355 (10) | C72—C73 | 1.376 (10) |
| C19—H19 | 0.9300 | C73—H73 | 0.9300 |
| C19—C20 | 1.403 (10) | C74—H74A | 0.9700 |
| C20—H20 | 0.9300 | C74—H74B | 0.9700 |
| C20—C21 | 1.378 (9) | C75—H75A | 0.9700 |
| C21—H21 | 0.9300 | C75—H75B | 0.9700 |
| C21—C22 | 1.401 (8) | C75—C76 | 1.515 (13) |
| C23—H23 | 0.9300 | C76—H76A | 0.9700 |
| C23—C24 | 1.386 (9) | C76—H76B | 0.9700 |
| C24—H24 | 0.9300 | C76—H76C | 0.9700 |
| C24—C25 | 1.375 (9) | C76—H76D | 0.9700 |
| C25—H25 | 0.9300 | C76—C77 | 1.549 (15) |
| C25—C26 | 1.368 (9) | C76—C77A | 1.604 (15) |
| C26—H26 | 0.9300 | C77—H77A | 0.9700 |
| C26—C27 | 1.403 (8) | C77—H77B | 0.9700 |
| C27—C28 | 1.463 (8) | C77—C78 | 1.457 (17) |
| C28—C29 | 1.417 (8) | C77A—H77C | 0.9700 |
| C28—C33 | 1.393 (8) | C77A—H77D | 0.9700 |
| C29—C30 | 1.402 (8) | C77A—C78A | 1.484 (17) |

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|---|---|---|---|
| C30—H30 | 0.9300 | C78—H78A | 0.9700 |
| C30—C31 | 1.394 (9) | C78—H78B | 0.9700 |
| C31—C32 | 1.386 (9) | C78—C79 | 1.542 (18) |
| C31—C34 | 1.506 (9) | C78A—H78C | 0.9700 |
| C32—H32 | 0.9300 | C78A—H78D | 0.9700 |
| C32—C33 | 1.390 (9) | C78A—C79A | 1.538 (18) |
| C33—H33 | 0.9300 | C79—H79A | 0.9700 |
| C34—H34A | 0.9700 | C79—H79B | 0.9700 |
| C34—H34B | 0.9700 | C79—C80 | 1.49 (3) |
| C35—H35A | 0.9700 | C79A—H79C | 0.9700 |
| C35—H35B | 0.9700 | C79A—H79D | 0.9700 |
| C35—C36 | 1.482 (13) | C79A—C80A | 1.46 (3) |
| C36—H36A | 0.9700 | C80—H80A | 0.9600 |
| C36—H36B | 0.9700 | C80—H80B | 0.9600 |
| C36—C37 | 1.561 (12) | C80—H80C | 0.9600 |
| C37—H37A | 0.9700 | C80A—H80D | 0.9600 |
| C37—H37B | 0.9700 | C80A—H80E | 0.9600 |
| C37—C38 | 1.447 (12) | C80A—H80F | 0.9600 |
| C38—H38A | 0.9700 | | |

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| N1—Ir1—N3 | 96.9 (2) | H38A—C38—H38B | 107.5 |
| N2—Ir1—N1 | 93.9 (2) | C39—C38—H38A | 108.5 |
| N2—Ir1—N3 | 93.27 (18) | C39—C38—H38B | 108.5 |
| C7—Ir1—N1 | 79.1 (2) | C38—C39—H39A | 108.0 |
| C7—Ir1—N2 | 89.6 (2) | C38—C39—H39B | 108.0 |
| C7—Ir1—N3 | 175.3 (2) | H39A—C39—H39B | 107.3 |
| C7—Ir1—C29 | 98.1 (2) | C40—C39—C38 | 117.1 (11) |
| C22—Ir1—N1 | 171.5 (2) | C40—C39—H39A | 108.0 |
| C22—Ir1—N2 | 79.4 (2) | C40—C39—H39B | 108.0 |
| C22—Ir1—N3 | 88.74 (19) | C39—C40—H40A | 109.5 |
| C22—Ir1—C7 | 95.5 (2) | C39—C40—H40B | 109.5 |
| C22—Ir1—C29 | 95.9 (2) | C39—C40—H40C | 109.5 |
| C29—Ir1—N1 | 91.4 (2) | H40A—C40—H40B | 109.5 |
| C29—Ir1—N2 | 171.3 (2) | H40A—C40—H40C | 109.5 |
| C29—Ir1—N3 | 79.3 (2) | H40B—C40—H40C | 109.5 |
| N6—Ir2—N5 | 93.7 (2) | N5—C41—H41 | 118.6 |
| N7—Ir2—N5 | 94.34 (19) | N5—C41—C42 | 122.7 (7) |
| N7—Ir2—N6 | 93.57 (19) | C42—C41—H41 | 118.6 |
| C47—Ir2—N5 | 79.3 (2) | C41—C42—H42 | 121.4 |
| C47—Ir2—N6 | 93.8 (2) | C41—C42—C43 | 117.3 (8) |
| C47—Ir2—N7 | 170.5 (2) | C43—C42—H42 | 121.4 |
| C58—Ir2—N5 | 171.6 (2) | C42—C43—H43 | 120.2 |
| C58—Ir2—N6 | 79.9 (2) | C44—C43—C42 | 119.5 (7) |
| C58—Ir2—N7 | 91.5 (2) | C44—C43—H43 | 120.2 |
| C58—Ir2—C47 | 95.6 (3) | C43—C44—H44 | 119.5 |
| C69—Ir2—N5 | 90.7 (2) | C43—C44—C45 | 121.1 (8) |
| C69—Ir2—N6 | 172.1 (2) | C45—C44—H44 | 119.5 |
| C69—Ir2—N7 | 79.6 (2) | N5—C45—C44 | 119.8 (7) |

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|---|---|---|---|
| C69—Ir2—C47 | 93.4 (2) | N5—C45—C46 | 114.3 (5) |
| C69—Ir2—C58 | 96.3 (3) | C44—C45—C46 | 125.9 (6) |
| C1—N1—Ir1 | 126.4 (5) | C47—C46—C45 | 116.2 (5) |
| C1—N1—C5 | 118.7 (6) | C47—C46—C51 | 121.4 (7) |
| C5—N1—Ir1 | 114.8 (5) | C51—C46—C45 | 122.4 (6) |
| C12—N2—Ir1 | 126.6 (5) | C46—C47—Ir2 | 115.5 (5) |
| C12—N2—C16 | 119.0 (6) | C46—C47—C48 | 117.1 (6) |
| C16—N2—Ir1 | 114.4 (4) | C48—C47—Ir2 | 127.3 (5) |
| C23—N3—Ir1 | 126.5 (4) | C47—C48—H48 | 119.5 |
| C23—N3—C27 | 119.1 (5) | C49—C48—C47 | 121.0 (7) |
| C27—N3—Ir1 | 114.3 (4) | C49—C48—H48 | 119.5 |
| H4A—N4—H4B | 107.4 | C48—C49—H49 | 119.3 |
| C34—N4—H4A | 108.3 | C50—C49—C48 | 121.4 (7) |
| C34—N4—H4B | 108.3 | C50—C49—H49 | 119.3 |
| C35—N4—H4A | 108.3 | C49—C50—H50 | 119.9 |
| C35—N4—H4B | 108.3 | C49—C50—C51 | 120.3 (7) |
| C35—N4—C34 | 115.8 (6) | C51—C50—H50 | 119.9 |
| C41—N5—Ir2 | 125.6 (5) | C46—C51—H51 | 120.6 |
| C41—N5—C45 | 119.5 (6) | C50—C51—C46 | 118.8 (7) |
| C45—N5—Ir2 | 114.7 (4) | C50—C51—H51 | 120.6 |
| C52—N6—Ir2 | 126.4 (5) | N6—C52—H52 | 119.0 |
| C52—N6—C56 | 119.2 (5) | N6—C52—C53 | 122.0 (7) |
| C56—N6—Ir2 | 114.2 (4) | C53—C52—H52 | 119.0 |
| C63—N7—Ir2 | 126.5 (4) | C52—C53—H53 | 120.6 |
| C63—N7—C67 | 117.5 (5) | C54—C53—C52 | 118.7 (8) |
| C67—N7—Ir2 | 115.9 (4) | C54—C53—H53 | 120.6 |
| H8A—N8—H8B | 107.3 | C53—C54—H54 | 119.9 |
| C74—N8—H8A | 108.2 | C55—C54—C53 | 120.2 (7) |
| C74—N8—H8B | 108.2 | C55—C54—H54 | 119.9 |
| C75—N8—H8A | 108.2 | C54—C55—H55 | 119.9 |
| C75—N8—H8B | 108.2 | C54—C55—C56 | 120.2 (7) |
| C75—N8—C74 | 116.5 (6) | C56—C55—H55 | 119.9 |
| N1—C1—H1 | 117.9 | N6—C56—C55 | 119.5 (7) |
| N1—C1—C2 | 124.3 (8) | N6—C56—C57 | 114.8 (5) |
| C2—C1—H1 | 117.9 | C55—C56—C57 | 125.7 (7) |
| C1—C2—H2 | 121.9 | C58—C57—C56 | 115.0 (6) |
| C3—C2—C1 | 116.1 (9) | C62—C57—C56 | 123.0 (7) |
| C3—C2—H2 | 121.9 | C62—C57—C58 | 121.9 (8) |
| C2—C3—H3 | 119.7 | C57—C58—Ir2 | 115.6 (5) |
| C4—C3—C2 | 120.6 (9) | C59—C58—Ir2 | 128.6 (5) |
| C4—C3—H3 | 119.7 | C59—C58—C57 | 115.9 (6) |
| C3—C4—H4 | 119.8 | C58—C59—H59 | 119.5 |
| C3—C4—C5 | 120.4 (8) | C58—C59—C60 | 121.1 (7) |
| C5—C4—H4 | 119.8 | C60—C59—H59 | 119.5 |
| N1—C5—C4 | 119.8 (7) | C59—C60—H60 | 119.5 |
| N1—C5—C6 | 113.6 (6) | C61—C60—C59 | 120.9 (8) |
| C4—C5—C6 | 126.6 (7) | C61—C60—H60 | 119.5 |
| C7—C6—C5 | 116.3 (6) | C60—C61—H61 | 120.2 |

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| C11—C6—C5 | 121.9 (7) | C60—C61—C62 | 119.5 (8) |
| C11—C6—C7 | 121.8 (7) | C62—C61—H61 | 120.2 |
| C6—C7—Ir1 | 115.5 (5) | C57—C62—H62 | 119.7 |
| C8—C7—Ir1 | 128.1 (5) | C61—C62—C57 | 120.6 (8) |
| C8—C7—C6 | 116.4 (6) | C61—C62—H62 | 119.7 |
| C7—C8—H8 | 119.3 | N7—C63—H63 | 118.0 |
| C9—C8—C7 | 121.4 (7) | N7—C63—C64 | 123.9 (6) |
| C9—C8—H8 | 119.3 | C64—C63—H63 | 118.0 |
| C8—C9—H9 | 119.5 | C63—C64—H64 | 120.8 |
| C10—C9—C8 | 121.0 (7) | C63—C64—C65 | 118.4 (6) |
| C10—C9—H9 | 119.5 | C65—C64—H64 | 120.8 |
| C9—C10—H10 | 120.1 | C64—C65—H65 | 120.3 |
| C9—C10—C11 | 119.9 (7) | C66—C65—C64 | 119.5 (6) |
| C11—C10—H10 | 120.1 | C66—C65—H65 | 120.3 |
| C6—C11—H11 | 120.3 | C65—C66—H66 | 119.9 |
| C10—C11—C6 | 119.4 (7) | C65—C66—C67 | 120.1 (6) |
| C10—C11—H11 | 120.3 | C67—C66—H66 | 119.9 |
| N2—C12—H12 | 119.0 | N7—C67—C66 | 120.5 (6) |
| N2—C12—C13 | 122.0 (7) | N7—C67—C68 | 113.3 (5) |
| C13—C12—H12 | 119.0 | C66—C67—C68 | 126.1 (6) |
| C12—C13—H13 | 120.4 | C69—C68—C67 | 115.2 (5) |
| C12—C13—C14 | 119.1 (7) | C73—C68—C67 | 123.2 (5) |
| C14—C13—H13 | 120.4 | C73—C68—C69 | 121.6 (6) |
| C13—C14—H14 | 120.5 | C68—C69—Ir2 | 115.8 (4) |
| C15—C14—C13 | 119.0 (7) | C70—C69—Ir2 | 128.2 (4) |
| C15—C14—H14 | 120.5 | C70—C69—C68 | 115.9 (5) |
| C14—C15—H15 | 119.3 | C69—C70—H70 | 118.5 |
| C14—C15—C16 | 121.5 (7) | C71—C70—C69 | 123.0 (5) |
| C16—C15—H15 | 119.3 | C71—C70—H70 | 118.5 |
| N2—C16—C15 | 119.4 (6) | C70—C71—C72 | 119.7 (6) |
| N2—C16—C17 | 114.0 (5) | C70—C71—C74 | 120.5 (6) |
| C15—C16—C17 | 126.5 (7) | C72—C71—C74 | 119.7 (6) |
| C18—C17—C16 | 122.4 (6) | C71—C72—H72 | 120.6 |
| C18—C17—C22 | 120.6 (6) | C73—C72—C71 | 118.7 (6) |
| C22—C17—C16 | 117.0 (6) | C73—C72—H72 | 120.6 |
| C17—C18—H18 | 119.9 | C68—C73—H73 | 119.5 |
| C19—C18—C17 | 120.2 (6) | C72—C73—C68 | 121.0 (6) |
| C19—C18—H18 | 119.9 | C72—C73—H73 | 119.5 |
| C18—C19—H19 | 119.7 | N8—C74—C71 | 112.8 (6) |
| C18—C19—C20 | 120.6 (6) | N8—C74—H74A | 109.0 |
| C20—C19—H19 | 119.7 | N8—C74—H74B | 109.0 |
| C19—C20—H20 | 120.3 | C71—C74—H74A | 109.0 |
| C21—C20—C19 | 119.3 (7) | C71—C74—H74B | 109.0 |
| C21—C20—H20 | 120.3 | H74A—C74—H74B | 107.8 |
| C20—C21—H21 | 118.8 | N8—C75—H75A | 109.7 |
| C20—C21—C22 | 122.5 (6) | N8—C75—H75B | 109.7 |
| C22—C21—H21 | 118.8 | N8—C75—C76 | 109.9 (6) |
| C17—C22—Ir1 | 114.6 (4) | H75A—C75—H75B | 108.2 |

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| C21—C22—Ir1 | 128.9 (4) | C76—C75—H75A | 109.7 |
| C21—C22—C17 | 116.6 (5) | C76—C75—H75B | 109.7 |
| N3—C23—H23 | 118.3 | C75—C76—H76A | 108.1 |
| N3—C23—C24 | 123.3 (6) | C75—C76—H76B | 108.1 |
| C24—C23—H23 | 118.3 | C75—C76—H76C | 110.6 |
| C23—C24—H24 | 121.0 | C75—C76—H76D | 110.6 |
| C25—C24—C23 | 118.1 (6) | C75—C76—C77 | 116.6 (9) |
| C25—C24—H24 | 121.0 | C75—C76—C77A | 105.8 (9) |
| C24—C25—H25 | 120.4 | H76A—C76—H76B | 107.3 |
| C26—C25—C24 | 119.3 (6) | H76C—C76—H76D | 108.7 |
| C26—C25—H25 | 120.4 | C77—C76—H76A | 108.1 |
| C25—C26—H26 | 119.7 | C77—C76—H76B | 108.1 |
| C25—C26—C27 | 120.5 (6) | C77A—C76—H76C | 110.6 |
| C27—C26—H26 | 119.7 | C77A—C76—H76D | 110.6 |
| N3—C27—C26 | 119.6 (5) | C76—C77—H77A | 109.3 |
| N3—C27—C28 | 115.2 (5) | C76—C77—H77B | 109.3 |
| C26—C27—C28 | 125.2 (5) | H77A—C77—H77B | 107.9 |
| C29—C28—C27 | 116.3 (5) | C78—C77—C76 | 111.8 (14) |
| C33—C28—C27 | 122.0 (5) | C78—C77—H77A | 109.3 |
| C33—C28—C29 | 121.7 (5) | C78—C77—H77B | 109.3 |
| C28—C29—Ir1 | 114.9 (4) | C76—C77A—H77C | 109.1 |
| C30—C29—Ir1 | 129.2 (4) | C76—C77A—H77D | 109.1 |
| C30—C29—C28 | 115.9 (5) | H77C—C77A—H77D | 107.9 |
| C29—C30—H30 | 118.8 | C78A—C77A—C76 | 112.4 (14) |
| C31—C30—C29 | 122.4 (6) | C78A—C77A—H77C | 109.1 |
| C31—C30—H30 | 118.8 | C78A—C77A—H77D | 109.1 |
| C30—C31—C34 | 119.1 (6) | C77—C78—H78A | 108.6 |
| C32—C31—C30 | 120.4 (6) | C77—C78—H78B | 108.6 |
| C32—C31—C34 | 120.2 (6) | C77—C78—C79 | 114.7 (17) |
| C31—C32—H32 | 120.6 | H78A—C78—H78B | 107.6 |
| C31—C32—C33 | 118.8 (6) | C79—C78—H78A | 108.6 |
| C33—C32—H32 | 120.6 | C79—C78—H78B | 108.6 |
| C28—C33—H33 | 119.6 | C77A—C78A—H78C | 109.5 |
| C32—C33—C28 | 120.8 (6) | C77A—C78A—H78D | 109.5 |
| C32—C33—H33 | 119.6 | C77A—C78A—C79A | 110.8 (18) |
| N4—C34—C31 | 114.0 (6) | H78C—C78A—H78D | 108.1 |
| N4—C34—H34A | 108.8 | C79A—C78A—H78C | 109.5 |
| N4—C34—H34B | 108.8 | C79A—C78A—H78D | 109.5 |
| C31—C34—H34A | 108.8 | C78—C79—H79A | 108.2 |
| C31—C34—H34B | 108.8 | C78—C79—H79B | 108.2 |
| H34A—C34—H34B | 107.7 | H79A—C79—H79B | 107.3 |
| N4—C35—H35A | 109.5 | C80—C79—C78 | 116.5 (18) |
| N4—C35—H35B | 109.5 | C80—C79—H79A | 108.2 |
| N4—C35—C36 | 110.7 (7) | C80—C79—H79B | 108.2 |
| H35A—C35—H35B | 108.1 | C78A—C79A—H79C | 108.3 |
| C36—C35—H35A | 109.5 | C78A—C79A—H79D | 108.3 |
| C36—C35—H35B | 109.5 | H79C—C79A—H79D | 107.4 |
| C35—C36—H36A | 109.6 | C80A—C79A—C78A | 116 (2) |

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| C35—C36—H36B | 109.6 | C80A—C79A—H79C | 108.3 |
| C35—C36—C37 | 110.2 (8) | C80A—C79A—H79D | 108.3 |
| H36A—C36—H36B | 108.1 | C79—C80—H80A | 109.5 |
| C37—C36—H36A | 109.6 | C79—C80—H80B | 109.5 |
| C37—C36—H36B | 109.6 | C79—C80—H80C | 109.5 |
| C36—C37—H37A | 109.0 | H80A—C80—H80B | 109.5 |
| C36—C37—H37B | 109.0 | H80A—C80—H80C | 109.5 |
| H37A—C37—H37B | 107.8 | H80B—C80—H80C | 109.5 |
| C38—C37—C36 | 113.0 (8) | C79A—C80A—H80D | 109.5 |
| C38—C37—H37A | 109.0 | C79A—C80A—H80E | 109.5 |
| C38—C37—H37B | 109.0 | C79A—C80A—H80F | 109.5 |
| C37—C38—H38A | 108.5 | H80D—C80A—H80E | 109.5 |
| C37—C38—H38B | 108.5 | H80D—C80A—H80F | 109.5 |
| C37—C38—C39 | 115.1 (10) | H80E—C80A—H80F | 109.5 |

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| Ir1—N1—C1—C2 | 175.2 (7) | C26—C27—C28—C33 | 2.0 (10) |
| Ir1—N1—C5—C4 | −173.2 (6) | C27—N3—C23—C24 | −2.4 (9) |
| Ir1—N1—C5—C6 | 6.7 (7) | C27—C28—C29—Ir1 | −3.7 (7) |
| Ir1—N2—C12—C13 | 177.5 (5) | C27—C28—C29—C30 | 178.9 (6) |
| Ir1—N2—C16—C15 | −178.4 (4) | C27—C28—C33—C32 | 179.7 (6) |
| Ir1—N2—C16—C17 | 2.2 (6) | C28—C29—C30—C31 | 0.7 (10) |
| Ir1—N3—C23—C24 | −178.9 (5) | C29—C28—C33—C32 | −2.3 (10) |
| Ir1—N3—C27—C26 | 178.2 (5) | C29—C30—C31—C32 | −0.7 (12) |
| Ir1—N3—C27—C28 | −1.0 (6) | C29—C30—C31—C34 | 173.9 (7) |
| Ir1—C7—C8—C9 | −175.6 (5) | C30—C31—C32—C33 | −0.7 (12) |
| Ir1—C29—C30—C31 | −176.2 (5) | C30—C31—C34—N4 | 141.8 (7) |
| Ir2—N5—C41—C42 | −175.2 (5) | C31—C32—C33—C28 | 2.2 (11) |
| Ir2—N5—C45—C44 | 177.4 (5) | C32—C31—C34—N4 | −43.7 (11) |
| Ir2—N5—C45—C46 | −2.3 (6) | C33—C28—C29—Ir1 | 178.2 (5) |
| Ir2—N6—C52—C53 | −172.1 (5) | C33—C28—C29—C30 | 0.8 (9) |
| Ir2—N6—C56—C55 | 172.4 (5) | C34—N4—C35—C36 | −176.5 (6) |
| Ir2—N6—C56—C57 | −6.4 (7) | C34—C31—C32—C33 | −175.3 (7) |
| Ir2—N7—C63—C64 | −176.5 (6) | C35—N4—C34—C31 | −59.9 (9) |
| Ir2—N7—C67—C66 | 177.4 (5) | C35—C36—C37—C38 | 177.3 (9) |
| Ir2—N7—C67—C68 | −3.0 (6) | C36—C37—C38—C39 | −171.4 (10) |
| Ir2—C47—C48—C49 | −175.7 (5) | C37—C38—C39—C40 | −62.2 (18) |
| Ir2—C58—C59—C60 | 179.8 (5) | C41—N5—C45—C44 | 2.1 (8) |
| Ir2—C69—C70—C71 | 173.1 (5) | C41—N5—C45—C46 | −177.7 (5) |
| N1—C1—C2—C3 | 0.3 (15) | C41—C42—C43—C44 | −2.3 (11) |
| N1—C5—C6—C7 | −1.3 (9) | C42—C43—C44—C45 | 4.1 (11) |
| N1—C5—C6—C11 | 177.6 (7) | C43—C44—C45—N5 | −4.0 (10) |
| N2—C12—C13—C14 | 1.2 (11) | C43—C44—C45—C46 | 175.8 (6) |
| N2—C16—C17—C18 | −179.1 (5) | C44—C45—C46—C47 | −177.2 (6) |
| N2—C16—C17—C22 | 4.2 (7) | C44—C45—C46—C51 | 4.2 (10) |
| N3—C23—C24—C25 | 2.1 (10) | C45—N5—C41—C42 | −0.4 (9) |
| N3—C27—C28—C29 | 3.1 (8) | C45—C46—C47—Ir2 | −1.5 (7) |
| N3—C27—C28—C33 | −178.8 (6) | C45—C46—C47—C48 | −177.9 (5) |
| N4—C35—C36—C37 | −176.9 (7) | C45—C46—C51—C50 | 177.4 (6) |

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| N5—C41—C42—C43 | 0.5 (10) | C46—C47—C48—C49 | 0.2 (9) |
| N5—C45—C46—C47 | 2.5 (7) | C47—C46—C51—C50 | −1.1 (10) |
| N5—C45—C46—C51 | −176.0 (6) | C47—C48—C49—C50 | −0.7 (10) |
| N6—C52—C53—C54 | 0.0 (12) | C48—C49—C50—C51 | 0.2 (12) |
| N6—C56—C57—C58 | 2.6 (8) | C49—C50—C51—C46 | 0.7 (12) |
| N6—C56—C57—C62 | −174.3 (6) | C51—C46—C47—Ir2 | 177.1 (5) |
| N7—C63—C64—C65 | −1.7 (12) | C51—C46—C47—C48 | 0.7 (9) |
| N7—C67—C68—C69 | 0.6 (8) | C52—N6—C56—C55 | −3.2 (9) |
| N7—C67—C68—C73 | 178.3 (6) | C52—N6—C56—C57 | 178.1 (6) |
| N8—C75—C76—C77 | −165.8 (10) | C52—C53—C54—C55 | −2.5 (12) |
| N8—C75—C76—C77A | 161.9 (11) | C53—C54—C55—C56 | 2.1 (12) |
| C1—N1—C5—C4 | 4.6 (11) | C54—C55—C56—N6 | 0.7 (10) |
| C1—N1—C5—C6 | −175.5 (6) | C54—C55—C56—C57 | 179.3 (7) |
| C1—C2—C3—C4 | −0.5 (16) | C55—C56—C57—C58 | −176.0 (6) |
| C2—C3—C4—C5 | 2.8 (16) | C55—C56—C57—C62 | 7.1 (10) |
| C3—C4—C5—N1 | −4.9 (13) | C56—N6—C52—C53 | 2.8 (10) |
| C3—C4—C5—C6 | 175.2 (9) | C56—C57—C58—Ir2 | 2.7 (7) |
| C4—C5—C6—C7 | 178.6 (7) | C56—C57—C58—C59 | −178.3 (6) |
| C4—C5—C6—C11 | −2.4 (12) | C56—C57—C62—C61 | 177.7 (7) |
| C5—N1—C1—C2 | −2.4 (12) | C57—C58—C59—C60 | 1.0 (10) |
| C5—C6—C7—Ir1 | −5.0 (8) | C58—C57—C62—C61 | 1.0 (11) |
| C5—C6—C7—C8 | 176.5 (6) | C58—C59—C60—C61 | −0.3 (12) |
| C5—C6—C11—C10 | −178.5 (7) | C59—C60—C61—C62 | −0.2 (13) |
| C6—C7—C8—C9 | 2.6 (9) | C60—C61—C62—C57 | −0.1 (13) |
| C7—C6—C11—C10 | 0.4 (11) | C62—C57—C58—Ir2 | 179.7 (5) |
| C7—C8—C9—C10 | −0.7 (10) | C62—C57—C58—C59 | −1.4 (9) |
| C8—C9—C10—C11 | −1.4 (11) | C63—N7—C67—C66 | −0.6 (9) |
| C9—C10—C11—C6 | 1.6 (12) | C63—N7—C67—C68 | 179.0 (6) |
| C11—C6—C7—Ir1 | 176.0 (6) | C63—C64—C65—C66 | 1.4 (12) |
| C11—C6—C7—C8 | −2.4 (10) | C64—C65—C66—C67 | −0.8 (11) |
| C12—N2—C16—C15 | −0.2 (8) | C65—C66—C67—N7 | 0.4 (10) |
| C12—N2—C16—C17 | −179.6 (5) | C65—C66—C67—C68 | −179.2 (6) |
| C12—C13—C14—C15 | −1.5 (11) | C66—C67—C68—C69 | −179.8 (6) |
| C13—C14—C15—C16 | 0.9 (11) | C66—C67—C68—C73 | −2.1 (10) |
| C14—C15—C16—N2 | −0.1 (10) | C67—N7—C63—C64 | 1.3 (10) |
| C14—C15—C16—C17 | 179.2 (6) | C67—C68—C69—Ir2 | 2.2 (7) |
| C15—C16—C17—C18 | 1.6 (9) | C67—C68—C69—C70 | 179.2 (5) |
| C15—C16—C17—C22 | −175.1 (6) | C67—C68—C73—C72 | −176.8 (6) |
| C16—N2—C12—C13 | −0.4 (10) | C68—C69—C70—C71 | −3.6 (9) |
| C16—C17—C18—C19 | −173.0 (6) | C69—C68—C73—C72 | 0.7 (10) |
| C16—C17—C22—Ir1 | −9.0 (6) | C69—C70—C71—C72 | 3.4 (10) |
| C16—C17—C22—C21 | 170.6 (5) | C69—C70—C71—C74 | −175.5 (6) |
| C17—C18—C19—C20 | 1.4 (9) | C70—C71—C72—C73 | −1.0 (10) |
| C18—C17—C22—Ir1 | 174.3 (4) | C70—C71—C74—N8 | 88.1 (8) |
| C18—C17—C22—C21 | −6.2 (8) | C71—C72—C73—C68 | −1.0 (11) |
| C18—C19—C20—C21 | −3.4 (9) | C72—C71—C74—N8 | −90.9 (8) |
| C19—C20—C21—C22 | 0.5 (9) | C73—C68—C69—Ir2 | −175.6 (5) |
| C20—C21—C22—Ir1 | −176.4 (4) | C73—C68—C69—C70 | 1.5 (9) |

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| C20—C21—C22—C17 | 4.2 (8) | C74—N8—C75—C76 | −176.3 (7) |
| C22—C17—C18—C19 | 3.6 (9) | C74—C71—C72—C73 | 178.0 (7) |
| C23—N3—C27—C26 | 1.3 (9) | C75—N8—C74—C71 | −58.0 (8) |
| C23—N3—C27—C28 | −177.9 (5) | C75—C76—C77—C78 | −178.8 (13) |
| C23—C24—C25—C26 | −0.6 (10) | C75—C76—C77A—C78A | −165.5 (15) |
| C24—C25—C26—C27 | −0.3 (10) | C76—C77—C78—C79 | 167.4 (15) |
| C25—C26—C27—N3 | 0.0 (10) | C76—C77A—C78A—C79A | −78 (2) |
| C25—C26—C27—C28 | 179.1 (6) | C77—C78—C79—C80 | 55 (3) |
| C26—C27—C28—C29 | −176.1 (6) | C77A—C78A—C79A—C80A | −71 (3) |

*Hydrogen-bond geometry (Å, º)*

Cg1–Cg6 are the centroids of the C6–C11, N2/C12–C16, C17–C22, C46–C51, C57–C62 and C68–C73 rings, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N4—H4*A*···Cl2$^{i}$ | 0.89 | 2.30 | 3.172 (6) | 168 |
| N4—H4*B*···Cl1$^{i}$ | 0.89 | 2.26 | 3.142 (6) | 172 |
| N8—H8*A*···Cl2 | 0.89 | 2.21 | 3.073 (6) | 165 |
| N8—H8*B*···Cl1 | 0.89 | 2.16 | 3.044 (6) | 171 |
| C20—H20···*Cg*1$^{ii}$ | 0.93 | 3.12 | 3.497 (7) | 145 |
| C24—H24···*Cg*4$^{iii}$ | 0.93 | 2.89 | 3.532 (7) | 139 |
| C26—H26···*Cg*5 | 0.93 | 2.79 | 3.645 (7) | 158 |
| C34—H34*B*···*Cg*3$^{ii}$ | 0.97 | 2.91 | 3.422 (7) | 160 |
| C37—H37···*Cg*1$^{ii}$ | 0.97 | 3.01 | 3.818 (7) | 141 |
| C49—H49···*Cg*2$^{iii}$ | 0.93 | 3.07 | 3.705 (7) | 145 |
| C53—H53···*Cg*6$^{iii}$ | 0.93 | 3.10 | 3.692 (7) | 135 |
| C65—H65···*Cg*3 | 0.93 | 2.86 | 3.530 (7) | 135 |

Symmetry codes: (i) *x*+1, −*y*+1/2, *z*+1/2; (ii) −*x*+2, −*y*+1, −*z*+1; (iii) *x*, −*y*+1/2, *z*−3/2.