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ISSN 2414-3146

# (2-Benzoyl-1-phenylethenolato-$\kappa^2O,O'$)bis[2-(1-phenyl-1*H*-benzimidazol-2-yl)phenyl-$\kappa C^1$]-iridium(III) dichloromethane disolvate

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Received 23 November 2016
Accepted 1 December 2016

Edited by M. Weil, Vienna University of Technology, Austria

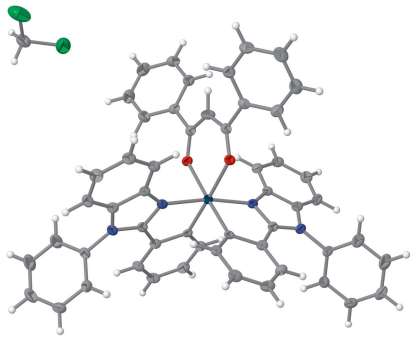
**Keywords:** crystal structure; iridium complexes; dibenzoylmethane; benzimidazole; *trans* effect.

**CCDC reference**: 1517541

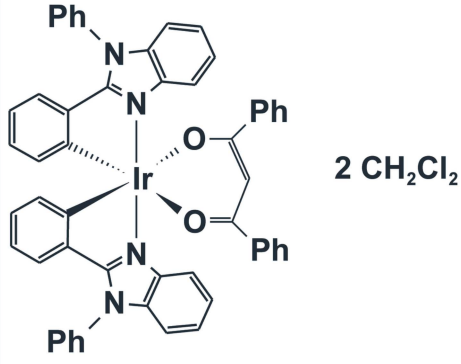
**Structural data**: full structural data are available from iucrdata.iucr.org

We present here synthesis and crystal structure of a neutral $Ir^{III}$ complex, $[Ir(C_{19}H_{13}N_2)_2(C_{15}H_{11}O_2)]\cdot 2CH_2Cl_2$ or $[Ir(C\text{^}N)_2O\text{^}O]\cdot 2CH_2Cl_2$, where C^N is 1,2-diphenyl-1*H*-benzimidazole and O^O is 2-benzoyl-1-phenylethenolate. The coordination sphere of the $Ir^{III}$ atom, located on a twofold rotation axis, is that of a slighlty distorted $C_2N_2O_2$ octahedron, with the N atoms in a *trans* configuration. In the crystal, complex molecules assemble through weak C—H$\cdots\pi$ interactions in the range 2.699 (3)–2.892 (3) Å. The solvent $CH_2Cl_2$ molecules reside in channels aligned along the *a* axis and are connected to the complex molecules by C—H$\cdots$O interactions.

3D view



Chemical scheme




## Structure description

Cyclometalated $Ir^{III}$ complexes with benzimidazole derivatives demonstrate unique optical properties, which have been intensively used in creating promising $Ir^{III}$-based luminescent and antitumor agents, as well as effective photosensitizers (Huang *et al.*, 2004; Yellol *et al.*, 2015). The title complex was synthesized in this context. Its molecular structure exhibits point-group symmetry *C*2, with the $Ir^{III}$ ion situated on the twofold rotation axis. The central ion shows a distorted octahedral $C_2N_2O_2$ coordination set formed by two bidentate C^N ligands and one bidentate O^O ligand (Fig. 1). The N atoms adopt a *trans* configuration other in this octahedron. The Ir—C [1.999 (4) Å] and Ir—N [2.041 (3) Å] bond lengths are significantly shorter than the Ir—O bond length [2.176 (3) Å], which is due to the *trans* effect exerted by the C-donor atoms of the coordinating C^N ligands. The dihedral angle between the planes of the benzimidazolyl and phenyl units of the C^N ligand is 2.6 (3)°, whereas the plane of the *N*-phenyl ring is inclined to the 2-phenyl-1*H*-benzimidazole plane by 80.3 (3)°. There are large channels in the crystal structure passing parallel to the *a* axis, which are filled by solvent $CH_2Cl_2$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C31—H31$A$···O1$^{i}$ | 0.99 | 2.39 | 3.377 (6) | 179 |

Symmetry code: (i) $-x, -y+\frac{1}{2}, z-\frac{1}{2}$.

molecules. These molecules form weak C—H···O hydrogen bonds with O atoms of the Ir$^{III}$ complex molecules with an almost ideal $D$—H···$A$ angle of 179° (Table 1). Other intermolecular interactions between complex molecules include weak C—H···$\pi$ interactions [range 2.699 (3)–2.892 (3) Å] involving phenyl H atoms and the centroids of the benzimidazole rings. The packing of the molecules is displayed in Fig. 2.

The structures of similar benzimidazole-based Ir$^{III}$ complexes have been reported by Bezzubov *et al.* (2014, 2016).

## Synthesis and crystallization

The title complex was synthesized by a two-step procedure. (i) $IrCl_3·3H_2O$ (80 mg, 0.25 mmol) and 1,2-diphenylbenzimidazole (259 mg, 0.96 mmol) in a mixture of 2-ethoxyethanol and water (3:1 *v*/*v*, 10 ml) were refluxed for 20 h under an argon atmosphere and cooled to room temperature. Distilled water (3 ml) was added and the precipitate which formed was collected by filtration, washed several times with water, ethanol and acetone, and dried *in vacuo* for 12 h. (ii) The crude $\mu$-chlorido-bridged iridium dimer (70 mg, 0.046 mmol), dibenzoylmethane (20.6 mg, 0.092 mmol) and $Na_2CO_3$ (50 mg, 0.47 mmol) in 2-ethoxyethanol (5 ml) were refluxed under an

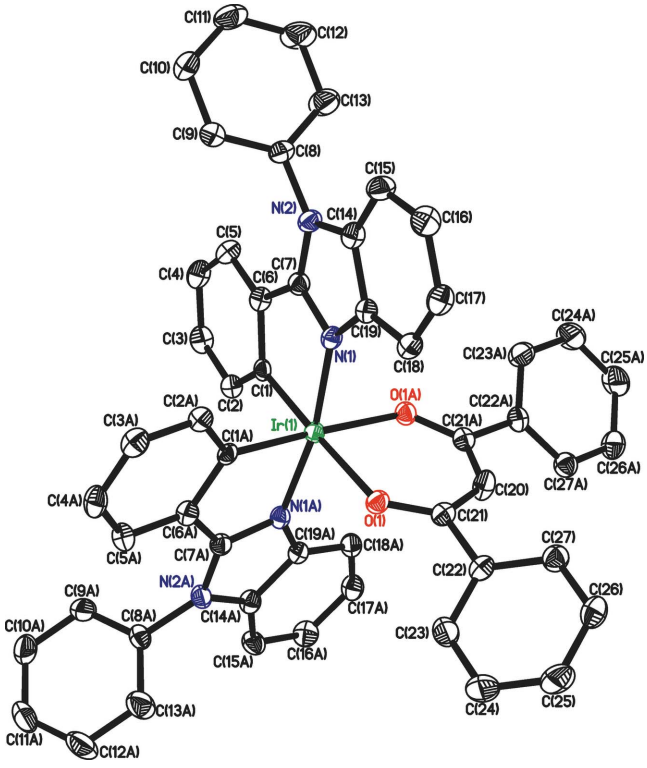



**Figure 1**
The molecular structure of [Ir(C^N)$_2$(O^O)]. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. The suffix A in atom labels indicates the symmetry operator ($-x$, $-y$, $z$). The solvent molecule is not shown.

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $[Ir(C_{19}H_{13}N_2)_2(C_{15}H_{11}O_2)]·2CH_2Cl_2$ |
| $M_r$ | 1123.92 |
| Crystal system, space group | Orthorhombic, *Aba*2 |
| Temperature (K) | 150 |
| *a*, *b*, *c* (Å) | 13.9159 (7), 25.5352 (12), 13.0898 (6) |
| *V* (Å$^3$) | 4651.4 (4) |
| *Z* | 4 |
| Radiation type | Mo *K*$\alpha$ |
| $\mu$ (mm$^{-1}$) | 3.15 |
| Crystal size (mm) | 0.40 × 0.25 × 0.15 |
| | |
| Data collection | |
| Diffractometer | Bruker SMART APEXII |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2008) |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 21901, 6169, 5029 |
| $R_{int}$ | 0.020 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.682 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.018, 0.043, 1.07 |
| No. of reflections | 6169 |
| No. of parameters | 299 |
| No. of restraints | 1 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 1.07, −0.46 |
| Absolute structure | Flack *x* determined using 2201 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013) |
| Absolute structure parameter | −0.007 (3) |

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXTL* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

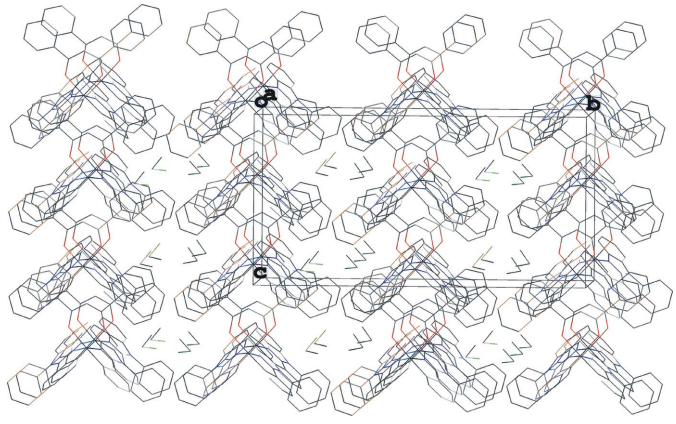



**Figure 2**
The crystal packing of the title complex.

argon atmosphere for 12 h and cooled to room temperature. Distilled water (2 ml) was added and the precipitate which formed was collected by filtration, washed several times with water and dried *in vacuo*. The orange solid was extracted with $CH_2Cl_2$ and the extract was purified by column chromatography ($SiO_2$, $CH_2Cl_2$/hexane 1:1 *v*/*v*) (yield: 47 mg, 54%). Single crystals of the desired complex were grown by slow evaporation of the solvent from a solution of the complex in $CH_2Cl_2$.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were placed in calculated positions and refined using a riding model, with C—H = 0.95–1.00 Å and $U_{iso}$(H) = 1.5$U_{eq}$(C) for methyl H atoms or 1.2$U_{eq}$(C) otherwise.

## Acknowledgements

This work was supported by RFBR (project No. 16-33-00604 'mol-a').

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# full crystallographic data

*IUCrData* (2016). **1**, x161915 [https://doi.org/10.1107/S2414314616019155]

## (2-Benzoyl-1-phenylethenolato-$\kappa^2O,O'$)bis[2-(1-phenyl-1*H*-benzimidazol-2-yl)phenyl-$\kappa C^1$]iridium(III) dichloromethane disolvate

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*Crystal data*

$[Ir(C_{19}H_{13}N_2)_2(C_{15}H_{11}O_2)]\cdot 2CH_2Cl_2$
$M_r$ = 1123.92
Orthorhombic, *Aba*2
$a$ = 13.9159 (7) Å
$b$ = 25.5352 (12) Å
$c$ = 13.0898 (6) Å
$V$ = 4651.4 (4) Å$^3$
$Z$ = 4
$F(000)$ = 2240
$D_x$ = 1.605 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 9873 reflections
$\theta$ = 2.2–30.5°
$\mu$ = 3.15 mm$^{-1}$
$T$ = 150 K
Plate, orange
0.40 × 0.25 × 0.15 mm

*Data collection*

Bruker SMART APEXII diffractometer
Radiation source: fine-focus sealed tube
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
21901 measured reflections
6169 independent reflections
5029 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.020
$\theta_{max}$ = 29.0°, $\theta_{min}$ = 2.2°
$h$ = −18→18
$k$ = −34→34
$l$ = −17→17

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.043
$S$ = 1.07
6169 reflections
299 parameters
1 restraint
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0163P)^2 + 6.3016P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.07 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.46 e Å$^{-3}$
Absolute structure: Flack $x$ determined using 2201 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: −0.007 (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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Ir1 | 0.0000 | 0.0000 | 0.87622 (4) | 0.01596 (4) |
| O1 | −0.0422 (2) | 0.05472 (12) | 0.7569 (2) | 0.0202 (6) |
| N1 | −0.12555 (19) | −0.04069 (10) | 0.8901 (2) | 0.0173 (6) |
| N2 | −0.2133 (2) | −0.10159 (12) | 0.9688 (2) | 0.0202 (6) |
| C1 | 0.0377 (3) | −0.05237 (16) | 0.9825 (3) | 0.0169 (8) |
| C2 | 0.1284 (3) | −0.06017 (15) | 1.0264 (3) | 0.0206 (7) |
| H6A | 0.1799 | −0.0378 | 1.0070 | 0.025* |
| C3 | 0.1456 (3) | −0.09984 (15) | 1.0979 (3) | 0.0250 (8) |
| H5A | 0.2084 | −0.1044 | 1.1250 | 0.030* |
| C4 | 0.0721 (3) | −0.13256 (18) | 1.1296 (3) | 0.0261 (10) |
| H4A | 0.0839 | −0.1586 | 1.1798 | 0.031* |
| C5 | −0.0197 (3) | −0.12704 (16) | 1.0873 (3) | 0.0238 (8) |
| H3A | −0.0704 | −0.1496 | 1.1076 | 0.029* |
| C6 | −0.0357 (3) | −0.08776 (15) | 1.0147 (3) | 0.0199 (7) |
| C7 | −0.1252 (3) | −0.07847 (14) | 0.9607 (3) | 0.0187 (7) |
| C8 | −0.2463 (3) | −0.14125 (14) | 1.0383 (3) | 0.0209 (7) |
| C9 | −0.2713 (3) | −0.12733 (17) | 1.1363 (3) | 0.0312 (10) |
| H15A | −0.2627 | −0.0923 | 1.1591 | 0.037* |
| C10 | −0.3093 (3) | −0.16477 (19) | 1.2019 (3) | 0.0385 (11) |
| H16A | −0.3261 | −0.1556 | 1.2699 | 0.046* |
| C11 | −0.3226 (3) | −0.21529 (18) | 1.1675 (4) | 0.0346 (10) |
| H17A | −0.3492 | −0.2409 | 1.2119 | 0.042* |
| C12 | −0.2977 (4) | −0.22885 (18) | 1.0693 (4) | 0.0403 (11) |
| H19A | −0.3065 | −0.2638 | 1.0464 | 0.048* |
| C13 | −0.2600 (3) | −0.19165 (17) | 1.0038 (3) | 0.0360 (10) |
| H18A | −0.2437 | −0.2008 | 0.9356 | 0.043* |
| C14 | −0.2745 (3) | −0.07636 (14) | 0.8998 (2) | 0.0208 (8) |
| C15 | −0.3710 (2) | −0.08408 (13) | 0.8788 (4) | 0.0246 (6) |
| H12A | −0.4077 | −0.1102 | 0.9127 | 0.029* |
| C16 | −0.4109 (3) | −0.05164 (17) | 0.8058 (3) | 0.0271 (8) |
| H11A | −0.4769 | −0.0555 | 0.7889 | 0.033* |
| C17 | −0.3568 (3) | −0.01333 (15) | 0.7562 (3) | 0.0244 (8) |
| H10A | −0.3870 | 0.0079 | 0.7060 | 0.029* |
| C18 | −0.2600 (3) | −0.00515 (14) | 0.7776 (3) | 0.0219 (7) |
| H9A | −0.2237 | 0.0213 | 0.7441 | 0.026* |
| C19 | −0.2191 (2) | −0.03793 (14) | 0.8509 (2) | 0.0179 (7) |
| C20 | 0.0000 | 0.0000 | 0.6161 (4) | 0.0263 (11) |
| H21A | 0.0000 | 0.0000 | 0.5435 | 0.032* |
| C21 | −0.0349 (3) | 0.04551 (14) | 0.6622 (3) | 0.0194 (7) |

| | | | | |
|---|---|---|---|---|
| C22 | −0.0652 (3) | 0.08839 (15) | 0.5905 (3) | 0.0213 (7) |
| C23 | −0.0429 (3) | 0.13971 (18) | 0.6134 (3) | 0.0290 (10) |
| H24A | −0.0113 | 0.1478 | 0.6759 | 0.035* |
| C24 | −0.0662 (4) | 0.17976 (18) | 0.5457 (4) | 0.0381 (11) |
| H25A | −0.0493 | 0.2149 | 0.5614 | 0.046* |
| C25 | −0.1137 (3) | 0.16867 (17) | 0.4558 (3) | 0.0362 (10) |
| H26A | −0.1301 | 0.1961 | 0.4100 | 0.043* |
| C26 | −0.1373 (3) | 0.11718 (17) | 0.4325 (3) | 0.0294 (9) |
| H27A | −0.1708 | 0.1094 | 0.3711 | 0.035* |
| C27 | −0.1123 (3) | 0.07730 (16) | 0.4986 (3) | 0.0243 (8) |
| H28A | −0.1272 | 0.0421 | 0.4815 | 0.029* |
| C31 | 0.1018 (3) | 0.32965 (17) | 0.3649 (4) | 0.0386 (11) |
| H31A | 0.0838 | 0.3634 | 0.3331 | 0.046* |
| H31B | 0.1283 | 0.3370 | 0.4336 | 0.046* |
| Cl1 | −0.00094 (11) | 0.28980 (5) | 0.3765 (3) | 0.0586 (3) |
| Cl2 | 0.18966 (10) | 0.29873 (7) | 0.28987 (11) | 0.0620 (4) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ir1 | 0.01740 (7) | 0.01518 (7) | 0.01531 (6) | 0.00053 (8) | 0.000 | 0.000 |
| O1 | 0.0239 (16) | 0.0183 (16) | 0.0183 (13) | 0.0011 (12) | 0.0007 (12) | 0.0014 (12) |
| N1 | 0.0189 (12) | 0.0176 (13) | 0.0153 (17) | 0.0023 (10) | −0.0004 (11) | 0.0010 (12) |
| N2 | 0.0207 (15) | 0.0215 (15) | 0.0184 (14) | −0.0016 (12) | −0.0006 (12) | 0.0039 (12) |
| C1 | 0.023 (2) | 0.015 (2) | 0.0127 (16) | 0.0016 (16) | 0.0002 (15) | −0.0030 (14) |
| C2 | 0.0211 (17) | 0.0209 (18) | 0.0200 (17) | 0.0011 (14) | −0.0008 (14) | −0.0009 (14) |
| C3 | 0.0244 (19) | 0.026 (2) | 0.0248 (19) | 0.0071 (15) | −0.0053 (15) | −0.0015 (15) |
| C4 | 0.029 (2) | 0.029 (2) | 0.0205 (18) | 0.0084 (17) | −0.0044 (16) | 0.0054 (16) |
| C5 | 0.025 (2) | 0.025 (2) | 0.0208 (17) | 0.0004 (14) | 0.0028 (14) | 0.0046 (15) |
| C6 | 0.0203 (16) | 0.0210 (19) | 0.0183 (17) | 0.0030 (15) | −0.0001 (14) | 0.0001 (14) |
| C7 | 0.0212 (17) | 0.0172 (17) | 0.0177 (17) | 0.0007 (13) | −0.0001 (13) | −0.0006 (14) |
| C8 | 0.0178 (16) | 0.0234 (18) | 0.0214 (17) | −0.0011 (14) | 0.0006 (13) | 0.0050 (15) |
| C9 | 0.039 (3) | 0.030 (2) | 0.025 (2) | −0.0131 (17) | 0.0054 (19) | −0.0043 (17) |
| C10 | 0.045 (3) | 0.050 (3) | 0.0197 (19) | −0.016 (2) | 0.0026 (18) | 0.0027 (19) |
| C11 | 0.035 (2) | 0.034 (2) | 0.035 (2) | −0.0056 (18) | 0.0003 (19) | 0.0153 (19) |
| C12 | 0.056 (3) | 0.019 (2) | 0.047 (3) | −0.003 (2) | 0.011 (2) | 0.0046 (19) |
| C13 | 0.048 (3) | 0.025 (2) | 0.034 (2) | −0.0034 (19) | 0.016 (2) | −0.0020 (18) |
| C14 | 0.0225 (17) | 0.0207 (17) | 0.019 (2) | 0.0036 (13) | −0.0003 (12) | 0.0006 (12) |
| C15 | 0.0214 (15) | 0.0263 (16) | 0.0261 (16) | −0.0036 (12) | 0.003 (2) | 0.003 (2) |
| C16 | 0.0193 (18) | 0.033 (2) | 0.029 (2) | 0.0011 (16) | −0.0023 (15) | 0.0007 (17) |
| C17 | 0.0247 (18) | 0.026 (2) | 0.0222 (17) | 0.0053 (14) | −0.0022 (15) | 0.0028 (14) |
| C18 | 0.0244 (17) | 0.0218 (19) | 0.0195 (15) | 0.0015 (15) | 0.0016 (13) | 0.0014 (15) |
| C19 | 0.0184 (16) | 0.0188 (16) | 0.0166 (17) | 0.0016 (13) | −0.0006 (11) | −0.0004 (12) |
| C20 | 0.034 (3) | 0.028 (3) | 0.017 (2) | 0.008 (3) | 0.000 | 0.000 |
| C21 | 0.0167 (15) | 0.0215 (18) | 0.0202 (16) | 0.0004 (14) | 0.0001 (14) | 0.0021 (14) |
| C22 | 0.0217 (17) | 0.0227 (19) | 0.0196 (16) | 0.0022 (14) | 0.0011 (14) | 0.0035 (14) |
| C23 | 0.035 (2) | 0.026 (2) | 0.026 (2) | −0.0007 (19) | −0.0047 (19) | −0.0026 (18) |
| C24 | 0.055 (3) | 0.021 (2) | 0.038 (2) | −0.0029 (19) | −0.007 (2) | 0.0073 (18) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C25 | 0.045 (3) | 0.028 (2) | 0.036 (2) | 0.0024 (19) | −0.006 (2) | 0.0135 (19) |
| C26 | 0.032 (2) | 0.034 (2) | 0.0227 (19) | 0.0030 (18) | −0.0063 (16) | 0.0050 (16) |
| C27 | 0.0248 (19) | 0.0247 (19) | 0.0235 (19) | 0.0007 (15) | −0.0011 (15) | 0.0016 (15) |
| C31 | 0.049 (2) | 0.033 (2) | 0.034 (3) | 0.0042 (17) | −0.008 (2) | −0.007 (2) |
| Cl1 | 0.0683 (7) | 0.0556 (6) | 0.0518 (6) | −0.0168 (7) | −0.0125 (7) | 0.0098 (18) |
| Cl2 | 0.0531 (8) | 0.0838 (11) | 0.0490 (7) | 0.0266 (8) | −0.0111 (6) | −0.0246 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ir1—C1$^{i}$ | 1.999 (4) | C12—H19A | 0.9500 |
| Ir1—C1 | 1.999 (4) | C13—H18A | 0.9500 |
| Ir1—N1$^{i}$ | 2.041 (3) | C14—C15 | 1.386 (5) |
| Ir1—N1 | 2.041 (3) | C14—C19 | 1.402 (5) |
| Ir1—O1$^{i}$ | 2.176 (3) | C15—C16 | 1.381 (6) |
| Ir1—O1 | 2.176 (3) | C15—H12A | 0.9500 |
| O1—C21 | 1.267 (5) | C16—C17 | 1.395 (6) |
| N1—C7 | 1.337 (4) | C16—H11A | 0.9500 |
| N1—C19 | 1.400 (4) | C17—C18 | 1.392 (5) |
| N2—C7 | 1.365 (5) | C17—H10A | 0.9500 |
| N2—C14 | 1.398 (4) | C18—C19 | 1.395 (5) |
| N2—C8 | 1.436 (5) | C18—H9A | 0.9500 |
| C1—C2 | 1.402 (6) | C20—C21$^{i}$ | 1.397 (4) |
| C1—C6 | 1.427 (6) | C20—C21 | 1.397 (4) |
| C2—C3 | 1.400 (5) | C20—H21A | 0.9500 |
| C2—H6A | 0.9500 | C21—C22 | 1.502 (5) |
| C3—C4 | 1.385 (6) | C22—C23 | 1.380 (6) |
| C3—H5A | 0.9500 | C22—C27 | 1.400 (5) |
| C4—C5 | 1.399 (5) | C23—C24 | 1.392 (6) |
| C4—H4A | 0.9500 | C23—H24A | 0.9500 |
| C5—C6 | 1.400 (5) | C24—C25 | 1.379 (6) |
| C5—H3A | 0.9500 | C24—H25A | 0.9500 |
| C6—C7 | 1.451 (5) | C25—C26 | 1.389 (6) |
| C8—C9 | 1.377 (5) | C25—H26A | 0.9500 |
| C8—C13 | 1.377 (5) | C26—C27 | 1.380 (5) |
| C9—C10 | 1.389 (6) | C26—H27A | 0.9500 |
| C9—H15A | 0.9500 | C27—H28A | 0.9500 |
| C10—C11 | 1.379 (7) | C31—Cl2 | 1.755 (5) |
| C10—H16A | 0.9500 | C31—Cl1 | 1.762 (5) |
| C11—C12 | 1.375 (7) | C31—H31A | 0.9900 |
| C11—H17A | 0.9500 | C31—H31B | 0.9900 |
| C12—C13 | 1.383 (6) | | |

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| C1$^{i}$—Ir1—C1 | 91.9 (2) | C11—C12—C13 | 120.1 (4) |
| C1$^{i}$—Ir1—N1$^{i}$ | 79.76 (15) | C11—C12—H19A | 119.9 |
| C1—Ir1—N1$^{i}$ | 93.11 (15) | C13—C12—H19A | 119.9 |
| C1$^{i}$—Ir1—N1 | 93.11 (15) | C8—C13—C12 | 119.4 (4) |
| C1—Ir1—N1 | 79.76 (15) | C8—C13—H18A | 120.3 |
| N1$^{i}$—Ir1—N1 | 169.81 (18) | C12—C13—H18A | 120.3 |

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| C1$^{i}$—Ir1—O1$^{i}$ | 177.96 (17) | C15—C14—N2 | 130.7 (4) |
| C1—Ir1—O1$^{i}$ | 89.94 (10) | C15—C14—C19 | 122.8 (3) |
| N1$^{i}$—Ir1—O1$^{i}$ | 99.17 (12) | N2—C14—C19 | 106.4 (3) |
| N1—Ir1—O1$^{i}$ | 88.17 (12) | C16—C15—C14 | 116.2 (4) |
| C1$^{i}$—Ir1—O1 | 89.94 (10) | C16—C15—H12A | 121.9 |
| C1—Ir1—O1 | 177.96 (17) | C14—C15—H12A | 121.9 |
| N1$^{i}$—Ir1—O1 | 88.17 (12) | C15—C16—C17 | 121.7 (4) |
| N1—Ir1—O1 | 99.17 (12) | C15—C16—H11A | 119.1 |
| O1$^{i}$—Ir1—O1 | 88.29 (16) | C17—C16—H11A | 119.1 |
| C21—O1—Ir1 | 124.2 (3) | C18—C17—C16 | 122.3 (4) |
| C7—N1—C19 | 107.0 (3) | C18—C17—H10A | 118.9 |
| C7—N1—Ir1 | 115.2 (2) | C16—C17—H10A | 118.9 |
| C19—N1—Ir1 | 137.5 (2) | C17—C18—C19 | 116.3 (3) |
| C7—N2—C14 | 107.3 (3) | C17—C18—H9A | 121.8 |
| C7—N2—C8 | 129.8 (3) | C19—C18—H9A | 121.8 |
| C14—N2—C8 | 122.6 (3) | C18—C19—N1 | 131.4 (3) |
| C2—C1—C6 | 115.7 (4) | C18—C19—C14 | 120.6 (3) |
| C2—C1—Ir1 | 128.1 (3) | N1—C19—C14 | 108.0 (3) |
| C6—C1—Ir1 | 116.2 (3) | C21$^{i}$—C20—C21 | 128.8 (5) |
| C3—C2—C1 | 122.1 (4) | C21$^{i}$—C20—H21A | 115.6 |
| C3—C2—H6A | 119.0 | C21—C20—H21A | 115.6 |
| C1—C2—H6A | 119.0 | O1—C21—C20 | 127.3 (4) |
| C4—C3—C2 | 120.7 (4) | O1—C21—C22 | 117.0 (3) |
| C4—C3—H5A | 119.6 | C20—C21—C22 | 115.8 (3) |
| C2—C3—H5A | 119.6 | C23—C22—C27 | 119.0 (4) |
| C3—C4—C5 | 119.7 (4) | C23—C22—C21 | 119.5 (4) |
| C3—C4—H4A | 120.2 | C27—C22—C21 | 121.4 (3) |
| C5—C4—H4A | 120.2 | C22—C23—C24 | 120.4 (4) |
| C4—C5—C6 | 119.1 (4) | C22—C23—H24A | 119.8 |
| C4—C5—H3A | 120.4 | C24—C23—H24A | 119.8 |
| C6—C5—H3A | 120.4 | C25—C24—C23 | 120.3 (4) |
| C5—C6—C1 | 122.7 (4) | C25—C24—H25A | 119.9 |
| C5—C6—C7 | 125.8 (4) | C23—C24—H25A | 119.9 |
| C1—C6—C7 | 111.5 (3) | C24—C25—C26 | 119.7 (4) |
| N1—C7—N2 | 111.2 (3) | C24—C25—H26A | 120.2 |
| N1—C7—C6 | 117.3 (3) | C26—C25—H26A | 120.2 |
| N2—C7—C6 | 131.5 (3) | C27—C26—C25 | 120.1 (4) |
| C9—C8—C13 | 120.8 (4) | C27—C26—H27A | 119.9 |
| C9—C8—N2 | 119.3 (3) | C25—C26—H27A | 119.9 |
| C13—C8—N2 | 119.7 (3) | C26—C27—C22 | 120.5 (4) |
| C8—C9—C10 | 119.6 (4) | C26—C27—H28A | 119.8 |
| C8—C9—H15A | 120.2 | C22—C27—H28A | 119.8 |
| C10—C9—H15A | 120.2 | Cl2—C31—Cl1 | 110.7 (3) |
| C11—C10—C9 | 119.6 (4) | Cl2—C31—H31A | 109.5 |
| C11—C10—H16A | 120.2 | Cl1—C31—H31A | 109.5 |
| C9—C10—H16A | 120.2 | Cl2—C31—H31B | 109.5 |
| C12—C11—C10 | 120.5 (4) | Cl1—C31—H31B | 109.5 |

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|---|---|---|---|
| C12—C11—H17A | 119.8 | H31A—C31—H31B | 108.1 |
| C10—C11—H17A | 119.8 | | |

Symmetry code: (i) −*x*, −*y*, *z*.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C31—H31*A*···O1$^{ii}$ | 0.99 | 2.39 | 3.377 (6) | 179 |

Symmetry code: (ii) −*x*, −*y*+1/2, *z*−1/2.