Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis(μ-diethyldithiocarbamato)bis[(η⁵-pentamethylcyclopentadienyl)-iridium(III)] bis(perchlorate)

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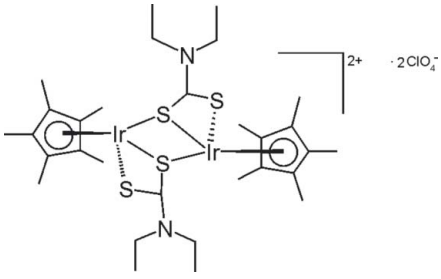
Received 28 June 2007; accepted 29 June 2007

Key indicators: single-crystal X-ray study; T = 108 K; mean σ(C–C) = 0.007 Å; R factor = 0.027; wR factor = 0.062; data-to-parameter ratio = 15.4.

Cations of the dinuclear title compound, $[Ir_2(C_{10}H_{15})_2(C_5H_{10}NS_2)_2](ClO_4)_2$, contain two half-sandwich $(\eta^5\text{-}C_5Me_5)Ir^{III}$ fragments and two tridentate diethyldithiocarbamate ligands, whose S atoms coordinate individual Ir^{III} atoms in a κ^2S,S'-fashion to afford four-membered chelate rings. The Ir^{III} atoms are linked by the thiocarbamate ligands in a μ-S bridging manner in a central $(IrS)_2$ ring. The $(\eta^5\text{-}C_5Me_5)Ir^{III}$ fragments adopt a *cis* arrangement relative to this ring and exhibit Ir—C distances in the range 2.167 (5)–2.206 (5) Å. Ir—S bond lengths to the bridging S atoms lie between 2.3897 (11) and 2.4098 (12) Å, and are slightly longer than those of 2.3842 (12) and 2.3832 (12) Å observed for the monodentate S atoms. The ions are linked by C—H···O hydrogen bonds.

Related literature

For related literature, see: Allen (2002); Butcher & Sinn (1976); Dean (1979); Gleichmann *et al.* (1995); Hendrickson *et al.* (1976); Herebian & Sheldrick (2002); Korn & Sheldrick (1997); Landgrafe & Sheldrick (1994); Lau *et al.* (2004); Raston & White (1976); Schäfer & Sheldrick (2007); Scharwitz *et al.* (2007*a*,*b*,*c*,*d*); Scharwitz, Schäfer *et al.* (2007); Sinn (1976); Stodt *et al.* (2003); Suzuki *et al.* (2003); Sheldrick (1995).



Experimental

Crystal data

$[Ir_2(C_{10}H_{15})_2(C_5H_{10}NS_2)_2](ClO_4)_2$
M_r = 1150.26
Orthorhombic, *Pbca*
a = 20.2386 (5) Å
b = 15.1259 (6) Å
c = 25.6234 (10) Å
V = 7844.0 (5) Å³
Z = 8
Mo $K\alpha$ radiation
μ = 7.18 mm⁻¹
T = 108 (2) K
0.46 × 0.30 × 0.12 mm

Data collection

Oxford diffraction Sapphire2 CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min} = 0.103, T_{max} = 0.416
37944 measured reflections
6895 independent reflections
5296 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.062
S = 1.03
6895 reflections
447 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.87 e Å⁻³
$\Delta\rho_{min}$ = −1.09 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Ir1—C35	2.167 (5)	Ir2—C41	2.174 (5)
Ir1—C31	2.173 (5)	Ir2—C45	2.175 (5)
Ir1—C34	2.191 (4)	Ir2—C44	2.182 (5)
Ir1—C32	2.193 (5)	Ir2—C42	2.189 (5)
Ir1—C33	2.206 (5)	Ir2—C43	2.195 (5)
Ir1—S22	2.3842 (12)	Ir2—S12	2.3832 (12)
Ir1—S21	2.3986 (12)	Ir2—S11	2.3897 (11)
Ir1—S11	2.4098 (12)	Ir2—S21	2.3952 (12)
S22—Ir1—S21	73.00 (4)	S12—Ir2—S21	94.83 (4)
S22—Ir1—S11	97.14 (4)	S11—Ir2—S21	80.31 (4)
S21—Ir1—S11	79.83 (4)	Ir2—S11—Ir1	99.54 (4)
S12—Ir2—S11	73.12 (4)	Ir2—S21—Ir1	99.71 (4)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C451—H452···O51^{i}	0.98	2.41	3.384 (6)	177
C25—H253···O61^{ii}	0.98	2.43	3.398 (7)	168

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2421).

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supplementary materials

Acta Cryst. (2007). E**63**, m2065-m2066 [**doi:10.1107/S1600536807031868**]

Bis(μ-diethyldithiocarbamato)bis[(η^5-pentamethylcyclopentadienyl)iridium(III)] bis(perchlorate)

M. Scharwitz, I. M. Oppel and W. S. Sheldrick

Comment

Entries for six (dithiocarbamato)iridium(III) complexes are present in the current Cambridge Structural Database (Version 5.27, December 2006; Allen 2002). These are all mononuclear and contain either one (Dean, 1979; Lau *et al.*, 2004; Suzuki *et al.*, 2003) or three (Butcher & Sinn, 1976; Raston & White, 1976; Sinn 1976) bidentate dithiocarbamato ligands in the chelating κ^2*S*,*S*' mode. We ourselves have also recently reported the first example of an (η^5-C_5Me_5)Ir^{III} complex to contain such a ligand, namely [(η^5-C_5Me_5)Ir{$(C_2H_5)_2NCS_2$-κ^2*S*,*S*'}(CO)](CF_3SO_3) (Scharwitz, Schäfer *et al.*, 2007*a*). This carbonyl complex was prepared by heating [(η^5-C_5Me_5)Ir{μ-$(C_2H_5)_2NCS_2$}]$_2$(CF_3SO_3)$_2$ (I) in methanol to 393 K in a sealed glass tube. We have now been successful in crystallizing the cation of dinuclear starting compound as its perchlorate [(η^5-C_5Me_5)Ir{μ-$(C_2H_5)_2NCS_2$}]$_2$(ClO_4)$_2$] (I) and report its structure as part of our continuing studies on (η^6-arene)Ru^{II} and (η^5-C_5Me_5)Ir^{III} complexes with sulfur and nitrogen containing ligands (Gleichmann *et al.*, 1995; Herebian & Sheldrick, 2002; Korn & Sheldrick, 1997; Schäfer & Sheldrick, 2007; Scharwitz *et al.*, 2007*a*, b, c, d); Scharwitz, Schäfer *et al.*, 2007; Stodt *et al.*, 2003).

The molecular structure of (I) is depicted in Fig. 1 and exhibits Ir—C distances to the pentamethylcyclopentadienyl ligands in the range 2.167 (5)–2.206 (5) as listed in Table 1. The (η^5-C_5Me_5)Ir^{III} fragments adopt a *cis* arrangement relative to the $(IrS)_2$ ring. Although the sulfur atoms S11 and S21 are bidentate, their Ir—S distances of respectively 2.4098 (12) and 2.3986 (12) Å to Ir1 and 2.3897 (11) and 2.3952 (12) Å to Ir2 are on average only marginally longer than those of 2.3842 (12) and 2.3832 (12) Å for the monodentate atoms S22 and S12. These latter values are similar to those of 2.3795 (12) and 2.3861 (14) Å reported for the Ir—S distances in the mononuclear carbonyl complex [(η^5-C_5Me_5)Ir{$(C_2H_5)_2NCS_2$-κ^2*S*,*S*'}(CO)](CF_3SO_3) (Scharwitz *et al.*, 2007*a*). This is also the case for the S—Ir—S angles of the chelate rings in (I), which exhibit values of 73.00 (4) and 73.12 (4) that are, on average only 0.46° larger than that of 72.60 (4)° in the carbonyl complex. Narrow S—Ir—S angles of 79.83 (4) and 80.31 (4)° are also observed for the Ir1 and Ir2 atoms within the central $(IrS)_2$ ring. (I) is the first iridium complex to contain tridentate dithiocarbamate ligands, although the observed 1κ^2*S*,*S*':2κ*S* coordination mode has previously been observed for later transition metals in [{Ru([9]aneS_3)}$_2${μ-$(C_2H_5)_2NCS_2$}$_2$] (Landgrafe & Sheldrick, 1994) and [Rh_2{$(CH_3)_2NCS_2$}$_5$](BF_4) (Hendrickson *et al.*, 1976). The cation and anion packing in the unit cell is illustrated in Fig. 2.

Experimental

[(η^5-C_5Me_5)Ir{μ-$(C_2H_5)_2NCS_2$}]$_2$(CF_3SO_3)$_2$ was prepared by reaction of [(η^5-C_5Me_5)Ir{$CH_3)_2CO$}$_3$](CF_3SO_3)$_2$ with Na[$(C_2H_5)_2NCS_2$] as described previously (Scharwitz *et al.*, 2007*a*). Suitable crystals [(η^5-C_5Me_5)Ir{μ-

$(C_2H_5)_2NCS_2\}]_2(ClO_4)_2]$ for X-ray analysis were obtained by slow evaporation of an aqueous solution of (I) containing 0.1*M* $NaClO_4$.

Refinement

H atoms were constrained to idealized positions and refined using a riding model, with C—H distances of 0.97 Å for the methylene C atoms and 0.96 Å for the methyl groups; U_{iso}(H) = 1.2 U_{iso}(C) for methylene and 1.5 U_{iso}(C) for methyl groups. The methyl groups were allowed to rotate but not to tip.

Figures

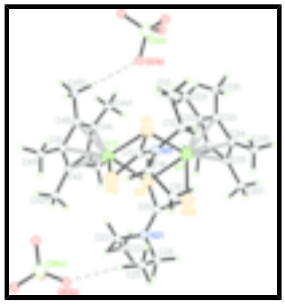


Fig. 1. Structure of the cation and counter anion of (I). Displacement ellipsoids are drawn at the 50% probability level.
Fig. 2. The crystal structure of (I) with the same colour code as in Fig.1.

Bis(μ-diethyldithiocarbamato)bis[(η^5– pentamethylcyclopentadienyl)iridium(III)] bis(perchlorate)

Crystal data

$[Ir_2(C_{10}H_{15})_2(C_5H_{10}NS_2)_2](ClO_4)_2$	F_{000} = 4480
M_r = 1150.26	D_x = 1.948 Mg m^{-3}
Orthorhombic, *Pbca*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 20169 reflections
a = 20.2386 (5) Å	θ = 2.6–30.0º
b = 15.1259 (6) Å	μ = 7.18 mm^{-1}
c = 25.6234 (10) Å	*T* = 108 (2) K
V = 7844.0 (5) Å^3	Prism, orange
Z = 8	0.46 × 0.30 × 0.12 mm

Data collection

Oxford diffraction Sapphire2 CCD diffractometer	6895 independent reflections
Radiation source: fine-focus sealed tube	5296 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.033
T = 108(2) K	θ_{max} = 25.0º
389 images at 1.0 deg in ω and 20 sec scans	θ_{min} = 2.6º
Absorption correction: multi-scan [empirical (using intensity measurements) correction (CrysAlis RED; Oxford Diffraction, 2006)]	*h* = −14→24

T_{min} = 0.103, T_{max} = 0.416
37944 measured reflections

k = −17→17
l = −30→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.062
S = 1.03
6895 reflections
447 parameters
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
$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.87 e Å^{-3}
$\Delta\rho_{min}$ = −1.09 e Å^{-3}
Extinction correction: none

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Ir1	0.557533 (8)	0.308853 (12)	0.106597 (7)	0.01081 (6)
Ir2	0.439865 (8)	0.150330 (12)	0.161882 (7)	0.01101 (6)
S11	0.52300 (6)	0.15748 (8)	0.09580 (5)	0.0129 (3)
S12	0.38394 (6)	0.15986 (9)	0.08023 (5)	0.0169 (3)
C11	0.4578 (2)	0.1599 (3)	0.04886 (18)	0.0129 (10)
N11	0.46949 (19)	0.1606 (3)	−0.00116 (15)	0.0160 (9)
C12	0.5375 (2)	0.1640 (4)	−0.0226 (2)	0.0210 (12)
H121	0.5651	0.2028	−0.0004	0.025*
H122	0.5363	0.1898	−0.0581	0.025*
C13	0.5687 (3)	0.0725 (4)	−0.0251 (2)	0.0274 (13)
H131	0.5709	0.0472	0.0100	0.041*
H132	0.6134	0.0772	−0.0396	0.041*
H133	0.5419	0.0341	−0.0476	0.041*
C14	0.4149 (3)	0.1599 (4)	−0.0391 (2)	0.0246 (13)
H141	0.3740	0.1396	−0.0216	0.030*
H142	0.4252	0.1175	−0.0674	0.030*

C15	0.4028 (3)	0.2507 (4)	−0.0628 (2)	0.0327 (14)
H151	0.3900	0.2922	−0.0352	0.049*
H152	0.3674	0.2468	−0.0887	0.049*
H153	0.4434	0.2716	−0.0796	0.049*
S21	0.46597 (6)	0.30463 (8)	0.16598 (5)	0.0129 (3)
S22	0.46610 (6)	0.37571 (9)	0.06318 (5)	0.0170 (3)
C21	0.4189 (2)	0.3592 (3)	0.11740 (19)	0.0148 (11)
N21	0.35764 (18)	0.3836 (3)	0.12422 (16)	0.0171 (9)
C22	0.3179 (2)	0.3544 (3)	0.1696 (2)	0.0202 (12)
H221	0.3330	0.2949	0.1804	0.024*
H222	0.2711	0.3495	0.1588	0.024*
C23	0.3228 (3)	0.4162 (4)	0.2153 (2)	0.0300 (14)
H231	0.3677	0.4145	0.2295	0.045*
H232	0.2913	0.3980	0.2423	0.045*
H233	0.3125	0.4765	0.2040	0.045*
C24	0.3239 (2)	0.4399 (3)	0.0852 (2)	0.0221 (12)
H241	0.3572	0.4753	0.0662	0.027*
H242	0.2939	0.4814	0.1034	0.027*
C25	0.2844 (3)	0.3861 (4)	0.0464 (2)	0.0331 (14)
H251	0.3143	0.3474	0.0268	0.050*
H252	0.2616	0.4260	0.0222	0.050*
H253	0.2518	0.3501	0.0650	0.050*
C31	0.6318 (2)	0.3742 (3)	0.1542 (2)	0.0181 (12)
C32	0.6563 (2)	0.2890 (3)	0.13970 (19)	0.0154 (11)
C33	0.6613 (2)	0.2883 (4)	0.08331 (19)	0.0192 (12)
C34	0.6392 (2)	0.3707 (3)	0.06404 (19)	0.0168 (11)
C35	0.6201 (2)	0.4251 (4)	0.1083 (2)	0.0219 (12)
C311	0.6221 (3)	0.4064 (4)	0.2084 (2)	0.0337 (15)
H311	0.6612	0.4399	0.2194	0.050*
H312	0.6157	0.3559	0.2317	0.050*
H313	0.5832	0.4448	0.2097	0.050*
C321	0.6833 (3)	0.2202 (4)	0.1754 (2)	0.0341 (15)
H321	0.7314	0.2271	0.1782	0.051*
H322	0.6730	0.1614	0.1616	0.051*
H323	0.6634	0.2269	0.2101	0.051*
C331	0.6905 (3)	0.2136 (4)	0.0526 (2)	0.0379 (16)
H331	0.6820	0.2230	0.0153	0.057*
H332	0.6703	0.1578	0.0636	0.057*
H333	0.7383	0.2112	0.0586	0.057*
C341	0.6386 (3)	0.3989 (5)	0.0078 (2)	0.0418 (17)
H341	0.6790	0.4321	0.0001	0.063*
H342	0.6000	0.4363	0.0013	0.063*
H343	0.6365	0.3464	−0.0146	0.063*
C351	0.5993 (3)	0.5189 (4)	0.1061 (3)	0.0470 (19)
H351	0.5691	0.5314	0.1351	0.070*
H352	0.5768	0.5303	0.0729	0.070*
H353	0.6383	0.5571	0.1089	0.070*
C41	0.3851 (2)	0.0371 (3)	0.19127 (19)	0.0170 (11)
C42	0.3713 (2)	0.1114 (3)	0.22381 (19)	0.0192 (11)

C43	0.4332 (3)	0.1377 (3)	0.24706 (19)	0.0201 (12)
C44	0.4841 (2)	0.0818 (3)	0.22816 (19)	0.0180 (11)
C45	0.4540 (2)	0.0182 (3)	0.19339 (18)	0.0156 (11)
C411	0.3344 (3)	−0.0136 (4)	0.1610 (2)	0.0265 (13)
H411	0.3545	−0.0374	0.1292	0.040*
H412	0.2978	0.0258	0.1516	0.040*
H413	0.3176	−0.0623	0.1825	0.040*
C421	0.3038 (3)	0.1449 (4)	0.2380 (2)	0.0334 (15)
H421	0.2753	0.1437	0.2071	0.050*
H422	0.3073	0.2058	0.2509	0.050*
H423	0.2848	0.1073	0.2653	0.050*
C431	0.4414 (3)	0.2102 (4)	0.2859 (2)	0.0348 (15)
H431	0.4311	0.1878	0.3209	0.052*
H432	0.4115	0.2589	0.2773	0.052*
H433	0.4872	0.2313	0.2852	0.052*
C441	0.5553 (2)	0.0821 (4)	0.2450 (2)	0.0286 (13)
H441	0.5692	0.1429	0.2525	0.043*
H442	0.5828	0.0578	0.2170	0.043*
H443	0.5603	0.0460	0.2765	0.043*
C451	0.4884 (3)	−0.0585 (4)	0.1689 (2)	0.0251 (13)
H451	0.4957	−0.1045	0.1951	0.038*
H452	0.5310	−0.0391	0.1547	0.038*
H453	0.4610	−0.0822	0.1406	0.038*
Cl5	0.70114 (6)	0.96099 (10)	0.12504 (6)	0.0292 (3)
O51	0.63858 (17)	1.0054 (3)	0.12472 (17)	0.0379 (11)
O52	0.74599 (19)	1.0063 (3)	0.15858 (17)	0.0448 (12)
O53	0.7257 (2)	0.9574 (4)	0.07341 (18)	0.0709 (18)
O54	0.6935 (3)	0.8735 (3)	0.1439 (2)	0.0734 (17)
Cl6	0.36173 (7)	0.71218 (10)	0.13784 (5)	0.0320 (3)
O61	0.3453 (2)	0.7734 (3)	0.09798 (17)	0.0506 (12)
O62	0.3582 (3)	0.7541 (3)	0.18724 (17)	0.0677 (16)
O63	0.3186 (4)	0.6423 (4)	0.1382 (2)	0.110 (3)
O64	0.4263 (3)	0.6801 (5)	0.1274 (2)	0.109 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ir1	0.00888 (10)	0.01305 (11)	0.01050 (10)	−0.00058 (8)	0.00031 (7)	0.00096 (7)
Ir2	0.01049 (10)	0.01253 (11)	0.01001 (10)	−0.00064 (8)	0.00088 (8)	0.00126 (7)
S11	0.0124 (6)	0.0141 (7)	0.0123 (6)	−0.0007 (5)	0.0027 (5)	0.0007 (5)
S12	0.0137 (6)	0.0223 (7)	0.0147 (7)	−0.0013 (5)	−0.0007 (5)	0.0007 (6)
C11	0.023 (3)	0.004 (2)	0.012 (3)	0.0036 (19)	−0.002 (2)	0.001 (2)
N11	0.018 (2)	0.017 (2)	0.014 (2)	−0.0029 (18)	0.0020 (17)	−0.0025 (18)
C12	0.020 (3)	0.028 (3)	0.015 (3)	−0.005 (2)	0.007 (2)	0.000 (2)
C13	0.035 (3)	0.029 (3)	0.018 (3)	0.003 (3)	0.010 (2)	−0.002 (2)
C14	0.025 (3)	0.032 (4)	0.017 (3)	−0.008 (2)	−0.003 (2)	−0.002 (2)
C15	0.036 (3)	0.041 (4)	0.021 (3)	−0.002 (3)	−0.007 (3)	0.005 (3)
S21	0.0110 (5)	0.0149 (7)	0.0130 (6)	−0.0005 (5)	−0.0002 (5)	0.0016 (5)

S22	0.0137 (6)	0.0219 (7)	0.0153 (7)	0.0012 (5)	−0.0003 (5)	0.0053 (5)
C21	0.019 (3)	0.009 (3)	0.016 (3)	−0.006 (2)	0.003 (2)	−0.002 (2)
N21	0.012 (2)	0.018 (2)	0.021 (2)	0.0003 (17)	−0.0023 (18)	0.0021 (19)
C22	0.015 (2)	0.018 (3)	0.028 (3)	0.004 (2)	0.006 (2)	0.006 (2)
C23	0.024 (3)	0.035 (4)	0.030 (3)	0.005 (3)	0.006 (3)	−0.001 (3)
C24	0.013 (2)	0.023 (3)	0.030 (3)	0.006 (2)	0.000 (2)	0.010 (2)
C25	0.027 (3)	0.042 (4)	0.030 (3)	0.000 (3)	−0.009 (3)	0.007 (3)
C31	0.009 (2)	0.023 (3)	0.022 (3)	−0.004 (2)	−0.002 (2)	−0.007 (2)
C32	0.008 (2)	0.017 (3)	0.022 (3)	−0.0021 (19)	0.000 (2)	−0.002 (2)
C33	0.010 (2)	0.033 (3)	0.015 (3)	−0.005 (2)	0.001 (2)	−0.006 (2)
C34	0.011 (2)	0.027 (3)	0.013 (3)	−0.008 (2)	−0.002 (2)	0.010 (2)
C35	0.012 (2)	0.019 (3)	0.034 (3)	−0.007 (2)	−0.005 (2)	0.008 (3)
C311	0.025 (3)	0.045 (4)	0.031 (4)	−0.009 (3)	0.007 (3)	−0.020 (3)
C321	0.029 (3)	0.032 (4)	0.041 (4)	0.001 (3)	−0.014 (3)	0.011 (3)
C331	0.019 (3)	0.050 (4)	0.044 (4)	0.002 (3)	0.008 (3)	−0.023 (3)
C341	0.029 (3)	0.068 (5)	0.028 (4)	−0.020 (3)	−0.005 (3)	0.021 (3)
C351	0.035 (4)	0.023 (4)	0.083 (6)	−0.003 (3)	−0.015 (4)	0.013 (3)
C41	0.018 (3)	0.017 (3)	0.016 (3)	−0.004 (2)	0.002 (2)	0.009 (2)
C42	0.022 (3)	0.019 (3)	0.017 (3)	0.001 (2)	0.011 (2)	0.006 (2)
C43	0.035 (3)	0.022 (3)	0.004 (2)	−0.005 (2)	0.002 (2)	0.003 (2)
C44	0.022 (3)	0.022 (3)	0.010 (3)	−0.004 (2)	−0.003 (2)	0.007 (2)
C45	0.020 (3)	0.017 (3)	0.010 (3)	0.000 (2)	0.003 (2)	0.004 (2)
C411	0.027 (3)	0.025 (3)	0.028 (3)	−0.010 (2)	−0.001 (2)	0.007 (3)
C421	0.029 (3)	0.030 (4)	0.041 (4)	0.007 (3)	0.020 (3)	0.014 (3)
C431	0.063 (4)	0.026 (3)	0.016 (3)	−0.009 (3)	0.000 (3)	0.001 (2)
C441	0.025 (3)	0.038 (4)	0.023 (3)	−0.006 (3)	−0.009 (2)	0.004 (3)
C451	0.031 (3)	0.020 (3)	0.025 (3)	0.004 (2)	0.007 (2)	0.004 (2)
Cl5	0.0211 (6)	0.0307 (8)	0.0360 (8)	0.0081 (6)	−0.0060 (6)	−0.0104 (7)
O51	0.0147 (18)	0.041 (3)	0.058 (3)	0.0088 (17)	−0.0031 (19)	−0.011 (2)
O52	0.029 (2)	0.048 (3)	0.057 (3)	0.009 (2)	−0.016 (2)	−0.023 (2)
O53	0.035 (3)	0.142 (6)	0.036 (3)	0.024 (3)	−0.002 (2)	−0.025 (3)
O54	0.078 (4)	0.038 (3)	0.104 (5)	−0.002 (3)	−0.035 (3)	0.008 (3)
Cl6	0.0430 (9)	0.0335 (9)	0.0196 (8)	0.0028 (7)	0.0031 (6)	0.0031 (6)
O61	0.053 (3)	0.065 (3)	0.034 (3)	0.010 (2)	0.002 (2)	0.019 (2)
O62	0.123 (5)	0.057 (4)	0.023 (3)	0.010 (3)	−0.003 (3)	−0.007 (2)
O63	0.171 (7)	0.078 (5)	0.082 (5)	−0.076 (5)	0.060 (5)	−0.034 (4)
O64	0.073 (4)	0.192 (8)	0.063 (4)	0.080 (4)	0.009 (3)	0.033 (4)

Geometric parameters (Å, °)

Ir1—C35	2.167 (5)	C32—C321	1.490 (7)
Ir1—C31	2.173 (5)	C33—C34	1.415 (7)
Ir1—C34	2.191 (4)	C33—C331	1.498 (7)
Ir1—C32	2.193 (5)	C34—C35	1.452 (7)
Ir1—C33	2.206 (5)	C34—C341	1.502 (7)
Ir1—S22	2.3842 (12)	C35—C351	1.481 (8)
Ir1—S21	2.3986 (12)	C311—H311	0.9800
Ir1—S11	2.4098 (12)	C311—H312	0.9800
Ir2—C41	2.174 (5)	C311—H313	0.9800

Ir2—C45	2.175 (5)	C321—H321	0.9800
Ir2—C44	2.182 (5)	C321—H322	0.9800
Ir2—C42	2.189 (5)	C321—H323	0.9800
Ir2—C43	2.195 (5)	C331—H331	0.9800
Ir2—S12	2.3832 (12)	C331—H332	0.9800
Ir2—S11	2.3897 (11)	C331—H333	0.9800
Ir2—S21	2.3952 (12)	C341—H341	0.9800
S11—C11	1.785 (5)	C341—H342	0.9800
S12—C11	1.698 (5)	C341—H343	0.9800
C11—N11	1.303 (6)	C351—H351	0.9800
N11—C14	1.473 (6)	C351—H352	0.9800
N11—C12	1.483 (6)	C351—H353	0.9800
C12—C13	1.523 (7)	C41—C45	1.425 (6)
C12—H121	0.9900	C41—C42	1.427 (7)
C12—H122	0.9900	C41—C411	1.498 (7)
C13—H131	0.9800	C42—C43	1.443 (7)
C13—H132	0.9800	C42—C421	1.501 (7)
C13—H133	0.9800	C43—C44	1.419 (7)
C14—C15	1.520 (7)	C43—C431	1.490 (7)
C14—H141	0.9900	C44—C45	1.446 (7)
C14—H142	0.9900	C44—C441	1.504 (7)
C15—H151	0.9800	C45—C451	1.490 (7)
C15—H152	0.9800	C411—H411	0.9800
C15—H153	0.9800	C411—H412	0.9800
S21—C21	1.772 (5)	C411—H413	0.9800
S22—C21	1.705 (5)	C421—H421	0.9800
C21—N21	1.305 (6)	C421—H422	0.9800
N21—C22	1.480 (6)	C421—H423	0.9800
N21—C24	1.481 (6)	C431—H431	0.9800
C22—C23	1.504 (7)	C431—H432	0.9800
C22—H221	0.9900	C431—H433	0.9800
C22—H222	0.9900	C441—H441	0.9800
C23—H231	0.9800	C441—H442	0.9800
C23—H232	0.9800	C441—H443	0.9800
C23—H233	0.9800	C451—H451	0.9800
C24—C25	1.513 (7)	C451—H452	0.9800
C24—H241	0.9900	C451—H453	0.9800
C24—H242	0.9900	Cl5—O53	1.414 (5)
C25—H251	0.9800	Cl5—O54	1.416 (5)
C25—H252	0.9800	Cl5—O52	1.425 (4)
C25—H253	0.9800	Cl5—O51	1.434 (4)
C31—C35	1.425 (7)	Cl6—O63	1.371 (6)
C31—C32	1.430 (7)	Cl6—O62	1.417 (5)
C31—C311	1.485 (7)	Cl6—O61	1.418 (4)
C32—C33	1.449 (7)	Cl6—O64	1.420 (5)
C35—Ir1—C31	38.35 (19)	C32—C31—Ir1	71.6 (3)
C35—Ir1—C34	38.93 (19)	C311—C31—Ir1	125.6 (3)
C31—Ir1—C34	64.07 (18)	C31—C32—C33	106.8 (4)
C35—Ir1—C32	64.58 (18)	C31—C32—C321	126.7 (5)

C31—Ir1—C32	38.23 (18)	C33—C32—C321	125.6 (5)
C34—Ir1—C32	64.09 (18)	C31—C32—Ir1	70.1 (3)
C35—Ir1—C33	64.11 (19)	C33—C32—Ir1	71.3 (3)
C31—Ir1—C33	63.71 (18)	C321—C32—Ir1	131.9 (4)
C34—Ir1—C33	37.54 (19)	C34—C33—C32	108.6 (4)
C32—Ir1—C33	38.45 (18)	C34—C33—C331	127.3 (5)
C35—Ir1—S22	96.82 (14)	C32—C33—C331	123.9 (5)
C31—Ir1—S22	127.29 (14)	C34—C33—Ir1	70.6 (3)
C34—Ir1—S22	99.91 (13)	C32—C33—Ir1	70.3 (3)
C32—Ir1—S22	161.16 (13)	C331—C33—Ir1	128.6 (4)
C33—Ir1—S22	132.28 (14)	C33—C34—C35	108.1 (4)
C35—Ir1—S21	117.42 (15)	C33—C34—C341	125.9 (5)
C31—Ir1—S21	101.01 (13)	C35—C34—C341	125.9 (5)
C34—Ir1—S21	155.54 (14)	C33—C34—Ir1	71.8 (3)
C32—Ir1—S21	117.10 (13)	C35—C34—Ir1	69.7 (3)
C33—Ir1—S21	154.63 (14)	C341—C34—Ir1	126.4 (3)
S22—Ir1—S21	73.00 (4)	C31—C35—C34	107.1 (4)
C35—Ir1—S11	160.47 (14)	C31—C35—C351	126.6 (5)
C31—Ir1—S11	134.19 (14)	C34—C35—C351	126.0 (5)
C34—Ir1—S11	124.59 (14)	C31—C35—Ir1	71.0 (3)
C32—Ir1—S11	100.28 (13)	C34—C35—Ir1	71.4 (3)
C33—Ir1—S11	96.37 (14)	C351—C35—Ir1	127.6 (4)
S22—Ir1—S11	97.14 (4)	C31—C311—H311	109.5
S21—Ir1—S11	79.83 (4)	C31—C311—H312	109.5
C41—Ir2—C45	38.26 (17)	H311—C311—H312	109.5
C41—Ir2—C44	64.23 (18)	C31—C311—H313	109.5
C45—Ir2—C44	38.75 (18)	H311—C311—H313	109.5
C41—Ir2—C42	38.17 (19)	H312—C311—H313	109.5
C45—Ir2—C42	64.36 (18)	C32—C321—H321	109.5
C44—Ir2—C42	64.41 (18)	C32—C321—H322	109.5
C41—Ir2—C43	63.62 (19)	H321—C321—H322	109.5
C45—Ir2—C43	63.84 (18)	C32—C321—H323	109.5
C44—Ir2—C43	37.82 (18)	H321—C321—H323	109.5
C42—Ir2—C43	38.44 (18)	H322—C321—H323	109.5
C41—Ir2—S12	96.30 (13)	C33—C331—H331	109.5
C45—Ir2—S12	116.36 (13)	C33—C331—H332	109.5
C44—Ir2—S12	155.08 (14)	H331—C331—H332	109.5
C42—Ir2—S12	110.58 (14)	C33—C331—H333	109.5
C43—Ir2—S12	148.09 (14)	H331—C331—H333	109.5
C41—Ir2—S11	129.79 (14)	H332—C331—H333	109.5
C45—Ir2—S11	102.22 (12)	C34—C341—H341	109.5
C44—Ir2—S11	106.51 (13)	C34—C341—H342	109.5
C42—Ir2—S11	166.50 (14)	H341—C341—H342	109.5
C43—Ir2—S11	138.76 (14)	C34—C341—H343	109.5
S12—Ir2—S11	73.12 (4)	H341—C341—H343	109.5
C41—Ir2—S21	149.84 (14)	H342—C341—H343	109.5
C45—Ir2—S21	148.24 (13)	C35—C351—H351	109.5
C44—Ir2—S21	109.79 (14)	C35—C351—H352	109.5
C42—Ir2—S21	111.73 (14)	H351—C351—H352	109.5

C43—Ir2—S21	93.15 (13)	C35—C351—H353	109.5
S12—Ir2—S21	94.83 (4)	H351—C351—H353	109.5
S11—Ir2—S21	80.31 (4)	H352—C351—H353	109.5
C11—S11—Ir2	87.60 (16)	C45—C41—C42	109.2 (4)
C11—S11—Ir1	105.81 (15)	C45—C41—C411	126.0 (5)
Ir2—S11—Ir1	99.54 (4)	C42—C41—C411	124.8 (4)
C11—S12—Ir2	89.84 (16)	C45—C41—Ir2	70.9 (3)
N11—C11—S12	128.7 (4)	C42—C41—Ir2	71.5 (3)
N11—C11—S11	121.9 (4)	C411—C41—Ir2	125.0 (3)
S12—C11—S11	109.4 (3)	C41—C42—C43	106.7 (4)
C11—N11—C14	120.9 (4)	C41—C42—C421	125.9 (5)
C11—N11—C12	122.2 (4)	C43—C42—C421	126.6 (5)
C14—N11—C12	116.9 (4)	C41—C42—Ir2	70.3 (3)
N11—C12—C13	111.7 (4)	C43—C42—Ir2	71.0 (3)
N11—C12—H121	109.3	C421—C42—Ir2	131.4 (4)
C13—C12—H121	109.3	C44—C43—C42	109.0 (4)
N11—C12—H122	109.3	C44—C43—C431	125.8 (5)
C13—C12—H122	109.3	C42—C43—C431	125.2 (5)
H121—C12—H122	107.9	C44—C43—Ir2	70.6 (3)
C12—C13—H131	109.5	C42—C43—Ir2	70.6 (3)
C12—C13—H132	109.5	C431—C43—Ir2	126.4 (4)
H131—C13—H132	109.5	C43—C44—C45	107.6 (4)
C12—C13—H133	109.5	C43—C44—C441	126.6 (5)
H131—C13—H133	109.5	C45—C44—C441	125.6 (5)
H132—C13—H133	109.5	C43—C44—Ir2	71.6 (3)
N11—C14—C15	112.2 (4)	C45—C44—Ir2	70.4 (3)
N11—C14—H141	109.2	C441—C44—Ir2	127.9 (4)
C15—C14—H141	109.2	C41—C45—C44	107.5 (4)
N11—C14—H142	109.2	C41—C45—C451	126.6 (5)
C15—C14—H142	109.2	C44—C45—C451	125.5 (4)
H141—C14—H142	107.9	C41—C45—Ir2	70.8 (3)
C14—C15—H151	109.5	C44—C45—Ir2	70.9 (3)
C14—C15—H152	109.5	C451—C45—Ir2	128.3 (3)
H151—C15—H152	109.5	C41—C411—H411	109.5
C14—C15—H153	109.5	C41—C411—H412	109.5
H151—C15—H153	109.5	H411—C411—H412	109.5
H152—C15—H153	109.5	C41—C411—H413	109.5
C21—S21—Ir2	107.73 (16)	H411—C411—H413	109.5
C21—S21—Ir1	87.57 (16)	H412—C411—H413	109.5
Ir2—S21—Ir1	99.71 (4)	C42—C421—H421	109.5
C21—S22—Ir1	89.59 (17)	C42—C421—H422	109.5
N21—C21—S22	126.9 (4)	H421—C421—H422	109.5
N21—C21—S21	123.3 (4)	C42—C421—H423	109.5
S22—C21—S21	109.8 (3)	H421—C421—H423	109.5
C21—N21—C22	122.5 (4)	H422—C421—H423	109.5
C21—N21—C24	120.7 (4)	C43—C431—H431	109.5
C22—N21—C24	116.8 (4)	C43—C431—H432	109.5
N21—C22—C23	113.1 (4)	H431—C431—H432	109.5
N21—C22—H221	109.0	C43—C431—H433	109.5

C23—C22—H221	109.0	H431—C431—H433	109.5
N21—C22—H222	109.0	H432—C431—H433	109.5
C23—C22—H222	109.0	C44—C441—H441	109.5
H221—C22—H222	107.8	C44—C441—H442	109.5
C22—C23—H231	109.5	H441—C441—H442	109.5
C22—C23—H232	109.5	C44—C441—H443	109.5
H231—C23—H232	109.5	H441—C441—H443	109.5
C22—C23—H233	109.5	H442—C441—H443	109.5
H231—C23—H233	109.5	C45—C451—H451	109.5
H232—C23—H233	109.5	C45—C451—H452	109.5
N21—C24—C25	112.2 (4)	H451—C451—H452	109.5
N21—C24—H241	109.2	C45—C451—H453	109.5
C25—C24—H241	109.2	H451—C451—H453	109.5
N21—C24—H242	109.2	H452—C451—H453	109.5
C25—C24—H242	109.2	O53—Cl5—O54	108.8 (4)
H241—C24—H242	107.9	O53—Cl5—O52	111.0 (3)
C24—C25—H251	109.5	O54—Cl5—O52	108.3 (3)
C24—C25—H252	109.5	O53—Cl5—O51	108.8 (3)
H251—C25—H252	109.5	O54—Cl5—O51	110.0 (3)
C24—C25—H253	109.5	O52—Cl5—O51	109.9 (2)
H251—C25—H253	109.5	O63—Cl6—O62	107.8 (3)
H252—C25—H253	109.5	O63—Cl6—O61	111.1 (4)
C35—C31—C32	109.3 (4)	O62—Cl6—O61	109.9 (3)
C35—C31—C311	124.9 (5)	O63—Cl6—O64	108.9 (5)
C32—C31—C311	125.7 (5)	O62—Cl6—O64	111.5 (4)
C35—C31—Ir1	70.6 (3)	O61—Cl6—O64	107.6 (3)
C41—Ir2—S11—C11	82.5 (2)	S11—Ir1—C34—C33	−47.4 (3)
C45—Ir2—S11—C11	112.6 (2)	C31—Ir1—C34—C35	−38.2 (3)
C44—Ir2—S11—C11	152.4 (2)	C32—Ir1—C34—C35	−80.9 (3)
C42—Ir2—S11—C11	106.4 (6)	C33—Ir1—C34—C35	−118.1 (4)
C43—Ir2—S11—C11	176.6 (2)	S22—Ir1—C34—C35	88.6 (3)
S12—Ir2—S11—C11	−1.57 (15)	S21—Ir1—C34—C35	18.0 (5)
S21—Ir2—S11—C11	−99.69 (15)	S11—Ir1—C34—C35	−165.5 (2)
C41—Ir2—S11—Ir1	−171.89 (16)	C35—Ir1—C34—C341	−120.2 (6)
C45—Ir2—S11—Ir1	−141.79 (13)	C31—Ir1—C34—C341	−158.4 (6)
C44—Ir2—S11—Ir1	−101.97 (14)	C32—Ir1—C34—C341	158.9 (6)
C42—Ir2—S11—Ir1	−147.9 (6)	C33—Ir1—C34—C341	121.7 (6)
C43—Ir2—S11—Ir1	−77.7 (2)	S22—Ir1—C34—C341	−31.6 (5)
S12—Ir2—S11—Ir1	104.06 (5)	S21—Ir1—C34—C341	−102.2 (5)
S21—Ir2—S11—Ir1	5.94 (4)	S11—Ir1—C34—C341	74.3 (5)
C35—Ir1—S11—C11	−122.3 (5)	C32—C31—C35—C34	−1.2 (5)
C31—Ir1—S11—C11	179.8 (2)	C311—C31—C35—C34	176.8 (4)
C34—Ir1—S11—C11	−94.3 (2)	Ir1—C31—C35—C34	−62.7 (3)
C32—Ir1—S11—C11	−159.8 (2)	C32—C31—C35—C351	−175.2 (5)
C33—Ir1—S11—C11	−121.1 (2)	C311—C31—C35—C351	2.8 (8)
S22—Ir1—S11—C11	13.02 (17)	Ir1—C31—C35—C351	123.3 (5)
S21—Ir1—S11—C11	84.25 (17)	C32—C31—C35—Ir1	61.5 (3)
C35—Ir1—S11—Ir2	147.5 (4)	C311—C31—C35—Ir1	−120.5 (5)
C31—Ir1—S11—Ir2	89.58 (18)	C33—C34—C35—C31	0.6 (5)

C34—Ir1—S11—Ir2	175.54 (15)	C341—C34—C35—C31	−176.7 (4)
C32—Ir1—S11—Ir2	110.02 (13)	Ir1—C34—C35—C31	62.5 (3)
C33—Ir1—S11—Ir2	148.70 (13)	C33—C34—C35—C351	174.6 (5)
S22—Ir1—S11—Ir2	−77.17 (5)	C341—C34—C35—C351	−2.7 (8)
S21—Ir1—S11—Ir2	−5.94 (4)	Ir1—C34—C35—C351	−123.5 (5)
C41—Ir2—S12—C11	−128.1 (2)	C33—C34—C35—Ir1	−61.9 (3)
C45—Ir2—S12—C11	−93.9 (2)	C341—C34—C35—Ir1	120.8 (5)
C44—Ir2—S12—C11	−91.3 (3)	C34—Ir1—C35—C31	−116.3 (4)
C42—Ir2—S12—C11	−164.6 (2)	C32—Ir1—C35—C31	−36.8 (3)
C43—Ir2—S12—C11	−176.1 (3)	C33—Ir1—C35—C31	−79.6 (3)
S11—Ir2—S12—C11	1.65 (16)	S22—Ir1—C35—C31	146.3 (3)
S21—Ir2—S12—C11	79.98 (16)	S21—Ir1—C35—C31	72.0 (3)
Ir2—S12—C11—N11	177.2 (4)	S11—Ir1—C35—C31	−78.3 (5)
Ir2—S12—C11—S11	−2.2 (2)	C31—Ir1—C35—C34	116.3 (4)
Ir2—S11—C11—N11	−177.2 (4)	C32—Ir1—C35—C34	79.5 (3)
Ir1—S11—C11—N11	83.5 (4)	C33—Ir1—C35—C34	36.7 (3)
Ir2—S11—C11—S12	2.2 (2)	S22—Ir1—C35—C34	−97.3 (3)
Ir1—S11—C11—S12	−97.0 (2)	S21—Ir1—C35—C34	−171.7 (2)
S12—C11—N11—C14	−1.2 (7)	S11—Ir1—C35—C34	38.0 (6)
S11—C11—N11—C14	178.2 (4)	C31—Ir1—C35—C351	−122.1 (7)
S12—C11—N11—C12	177.6 (4)	C34—Ir1—C35—C351	121.6 (7)
S11—C11—N11—C12	−3.0 (7)	C32—Ir1—C35—C351	−158.8 (6)
C11—N11—C12—C13	83.6 (6)	C33—Ir1—C35—C351	158.3 (6)
C14—N11—C12—C13	−97.6 (5)	S22—Ir1—C35—C351	24.3 (5)
C11—N11—C14—C15	102.9 (5)	S21—Ir1—C35—C351	−50.1 (6)
C12—N11—C14—C15	−76.0 (6)	S11—Ir1—C35—C351	159.7 (4)
C41—Ir2—S21—C21	−98.7 (3)	C44—Ir2—C41—C45	−38.2 (3)
C45—Ir2—S21—C21	−177.8 (3)	C42—Ir2—C41—C45	−118.9 (4)
C44—Ir2—S21—C21	−171.3 (2)	C43—Ir2—C41—C45	−80.5 (3)
C42—Ir2—S21—C21	−101.8 (2)	S12—Ir2—C41—C45	125.6 (3)
C43—Ir2—S21—C21	−136.4 (2)	S11—Ir2—C41—C45	52.3 (3)
S12—Ir2—S21—C21	12.64 (17)	S21—Ir2—C41—C45	−123.4 (3)
S11—Ir2—S21—C21	84.57 (17)	C45—Ir2—C41—C42	118.9 (4)
C41—Ir2—S21—Ir1	170.7 (3)	C44—Ir2—C41—C42	80.7 (3)
C45—Ir2—S21—Ir1	91.6 (2)	C43—Ir2—C41—C42	38.4 (3)
C44—Ir2—S21—Ir1	98.20 (14)	S12—Ir2—C41—C42	−115.6 (3)
C42—Ir2—S21—Ir1	167.67 (14)	S11—Ir2—C41—C42	171.2 (2)
C43—Ir2—S21—Ir1	133.02 (14)	S21—Ir2—C41—C42	−4.6 (4)
S12—Ir2—S21—Ir1	−77.91 (4)	C45—Ir2—C41—C411	−121.1 (6)
S11—Ir2—S21—Ir1	−5.97 (4)	C44—Ir2—C41—C411	−159.3 (5)
C35—Ir1—S21—C21	88.0 (2)	C42—Ir2—C41—C411	120.0 (5)
C31—Ir1—S21—C21	125.0 (2)	C43—Ir2—C41—C411	158.4 (5)
C34—Ir1—S21—C21	75.4 (3)	S12—Ir2—C41—C411	4.4 (4)
C32—Ir1—S21—C21	161.9 (2)	S11—Ir2—C41—C411	−68.8 (5)
C33—Ir1—S21—C21	175.0 (3)	S21—Ir2—C41—C411	115.5 (4)
S22—Ir1—S21—C21	−0.88 (16)	C45—C41—C42—C43	−0.9 (5)
S11—Ir1—S21—C21	−101.65 (16)	C411—C41—C42—C43	177.7 (4)
C35—Ir1—S21—Ir2	−164.37 (15)	Ir2—C41—C42—C43	−62.1 (3)
C31—Ir1—S21—Ir2	−127.42 (15)	C45—C41—C42—C421	−171.3 (5)

C34—Ir1—S21—Ir2	−177.0 (3)	C411—C41—C42—C421	7.2 (8)
C32—Ir1—S21—Ir2	−90.50 (15)	Ir2—C41—C42—C421	127.5 (5)
C33—Ir1—S21—Ir2	−77.4 (3)	C45—C41—C42—Ir2	61.2 (3)
S22—Ir1—S21—Ir2	106.70 (5)	C411—C41—C42—Ir2	−120.3 (5)
S11—Ir1—S21—Ir2	5.93 (4)	C45—Ir2—C42—C41	−37.0 (3)
C35—Ir1—S22—C21	−115.7 (2)	C44—Ir2—C42—C41	−80.2 (3)
C31—Ir1—S22—C21	−90.1 (2)	C43—Ir2—C42—C41	−116.5 (4)
C34—Ir1—S22—C21	−155.0 (2)	S12—Ir2—C42—C41	73.3 (3)
C32—Ir1—S22—C21	−124.5 (4)	S11—Ir2—C42—C41	−30.3 (8)
C33—Ir1—S22—C21	−176.7 (2)	S21—Ir2—C42—C41	177.5 (2)
S21—Ir1—S22—C21	0.91 (16)	C41—Ir2—C42—C43	116.5 (4)
S11—Ir1—S22—C21	77.95 (16)	C45—Ir2—C42—C43	79.5 (3)
Ir1—S22—C21—N21	177.4 (4)	C44—Ir2—C42—C43	36.3 (3)
Ir1—S22—C21—S21	−1.3 (2)	S12—Ir2—C42—C43	−170.2 (3)
Ir2—S21—C21—N21	83.1 (4)	S11—Ir2—C42—C43	86.2 (7)
Ir1—S21—C21—N21	−177.5 (4)	S21—Ir2—C42—C43	−66.0 (3)
Ir2—S21—C21—S22	−98.2 (2)	C41—Ir2—C42—C421	−121.0 (6)
Ir1—S21—C21—S22	1.2 (2)	C45—Ir2—C42—C421	−158.0 (6)
S22—C21—N21—C22	170.6 (4)	C44—Ir2—C42—C421	158.8 (6)
S21—C21—N21—C22	−11.0 (7)	C43—Ir2—C42—C421	122.5 (7)
S22—C21—N21—C24	−7.2 (7)	S12—Ir2—C42—C421	−47.7 (5)
S21—C21—N21—C24	171.3 (4)	S11—Ir2—C42—C421	−151.3 (5)
C21—N21—C22—C23	90.6 (6)	S21—Ir2—C42—C421	56.5 (5)
C24—N21—C22—C23	−91.6 (5)	C41—C42—C43—C44	1.3 (6)
C21—N21—C24—C25	94.9 (5)	C421—C42—C43—C44	171.6 (5)
C22—N21—C24—C25	−83.0 (5)	Ir2—C42—C43—C44	−60.4 (3)
C34—Ir1—C31—C35	38.8 (3)	C41—C42—C43—C431	−176.9 (5)
C32—Ir1—C31—C35	119.1 (4)	C421—C42—C43—C431	−6.6 (8)
C33—Ir1—C31—C35	80.8 (3)	Ir2—C42—C43—C431	121.4 (5)
S22—Ir1—C31—C35	−43.8 (3)	C41—C42—C43—Ir2	61.7 (3)
S21—Ir1—C31—C35	−120.7 (3)	C421—C42—C43—Ir2	−128.0 (5)
S11—Ir1—C31—C35	152.8 (2)	C41—Ir2—C43—C44	81.2 (3)
C35—Ir1—C31—C32	−119.1 (4)	C45—Ir2—C43—C44	38.4 (3)
C34—Ir1—C31—C32	−80.3 (3)	C42—Ir2—C43—C44	119.4 (4)
C33—Ir1—C31—C32	−38.3 (3)	S12—Ir2—C43—C44	136.8 (3)
S22—Ir1—C31—C32	−162.9 (2)	S11—Ir2—C43—C44	−40.0 (4)
S21—Ir1—C31—C32	120.2 (3)	S21—Ir2—C43—C44	−118.8 (3)
S11—Ir1—C31—C32	33.7 (4)	C41—Ir2—C43—C42	−38.1 (3)
C35—Ir1—C31—C311	119.6 (6)	C45—Ir2—C43—C42	−81.0 (3)
C34—Ir1—C31—C311	158.4 (5)	C44—Ir2—C43—C42	−119.4 (4)
C32—Ir1—C31—C311	−121.3 (6)	S12—Ir2—C43—C42	17.5 (4)
C33—Ir1—C31—C311	−159.6 (5)	S11—Ir2—C43—C42	−159.3 (2)
S22—Ir1—C31—C311	75.8 (5)	S21—Ir2—C43—C42	121.8 (3)
S21—Ir1—C31—C311	−1.1 (5)	C41—Ir2—C43—C431	−158.0 (5)
S11—Ir1—C31—C311	−87.6 (5)	C45—Ir2—C43—C431	159.1 (5)
C35—C31—C32—C33	1.4 (5)	C44—Ir2—C43—C431	120.7 (6)
C311—C31—C32—C33	−176.6 (4)	C42—Ir2—C43—C431	−119.9 (6)
Ir1—C31—C32—C33	62.2 (3)	S12—Ir2—C43—C431	−102.4 (5)
C35—C31—C32—C321	171.1 (5)	S11—Ir2—C43—C431	80.8 (5)

C311—C31—C32—C321	−6.9 (8)	S21—Ir2—C43—C431	1.9 (5)
Ir1—C31—C32—C321	−128.1 (5)	C42—C43—C44—C45	−1.2 (5)
C35—C31—C32—Ir1	−60.8 (3)	C431—C43—C44—C45	177.0 (5)
C311—C31—C32—Ir1	121.2 (5)	Ir2—C43—C44—C45	−61.5 (3)
C35—Ir1—C32—C31	36.9 (3)	C42—C43—C44—C441	−175.6 (5)
C34—Ir1—C32—C31	80.3 (3)	C431—C43—C44—C441	2.6 (8)
C33—Ir1—C32—C31	116.6 (4)	Ir2—C43—C44—C441	124.0 (5)
S22—Ir1—C32—C31	46.5 (6)	C42—C43—C44—Ir2	60.4 (3)
S21—Ir1—C32—C31	−72.4 (3)	C431—C43—C44—Ir2	−121.4 (5)
S11—Ir1—C32—C31	−156.1 (3)	C41—Ir2—C44—C43	−79.5 (3)
C35—Ir1—C32—C33	−79.7 (3)	C45—Ir2—C44—C43	−117.1 (4)
C31—Ir1—C32—C33	−116.6 (4)	C42—Ir2—C44—C43	−36.9 (3)
C34—Ir1—C32—C33	−36.3 (3)	S12—Ir2—C44—C43	−120.9 (3)
S22—Ir1—C32—C33	−70.1 (5)	S11—Ir2—C44—C43	153.8 (3)
S21—Ir1—C32—C33	171.0 (2)	S21—Ir2—C44—C43	68.4 (3)
S11—Ir1—C32—C33	87.3 (3)	C41—Ir2—C44—C45	37.7 (3)
C35—Ir1—C32—C321	158.8 (6)	C42—Ir2—C44—C45	80.2 (3)
C31—Ir1—C32—C321	122.0 (6)	C43—Ir2—C44—C45	117.1 (4)
C34—Ir1—C32—C321	−157.8 (6)	S12—Ir2—C44—C45	−3.7 (5)
C33—Ir1—C32—C321	−121.5 (6)	S11—Ir2—C44—C45	−89.1 (3)
S22—Ir1—C32—C321	168.4 (4)	S21—Ir2—C44—C45	−174.5 (2)
S21—Ir1—C32—C321	49.6 (5)	C41—Ir2—C44—C441	158.1 (5)
S11—Ir1—C32—C321	−34.2 (5)	C45—Ir2—C44—C441	120.4 (6)
C31—C32—C33—C34	−1.0 (5)	C42—Ir2—C44—C441	−159.4 (5)
C321—C32—C33—C34	−170.8 (5)	C43—Ir2—C44—C441	−122.5 (6)
Ir1—C32—C33—C34	60.5 (3)	S12—Ir2—C44—C441	116.7 (5)
C31—C32—C33—C331	174.6 (4)	S11—Ir2—C44—C441	31.3 (5)
C321—C32—C33—C331	4.7 (8)	S21—Ir2—C44—C441	−54.1 (5)
Ir1—C32—C33—C331	−123.9 (5)	C42—C41—C45—C44	0.2 (5)
C31—C32—C33—Ir1	−61.5 (3)	C411—C41—C45—C44	−178.3 (4)
C321—C32—C33—Ir1	128.7 (5)	Ir2—C41—C45—C44	61.7 (3)
C35—Ir1—C33—C34	−38.0 (3)	C42—C41—C45—C451	174.4 (5)
C31—Ir1—C33—C34	−80.9 (3)	C411—C41—C45—C451	−4.1 (8)
C32—Ir1—C33—C34	−119.1 (4)	Ir2—C41—C45—C451	−124.0 (5)
S22—Ir1—C33—C34	36.7 (3)	C42—C41—C45—Ir2	−61.6 (3)
S21—Ir1—C33—C34	−137.9 (3)	C411—C41—C45—Ir2	119.9 (5)
S11—Ir1—C33—C34	142.4 (3)	C43—C44—C45—C41	0.6 (5)
C35—Ir1—C33—C32	81.0 (3)	C441—C44—C45—C41	175.1 (5)
C31—Ir1—C33—C32	38.1 (3)	Ir2—C44—C45—C41	−61.7 (3)
C34—Ir1—C33—C32	119.1 (4)	C43—C44—C45—C451	−173.7 (5)
S22—Ir1—C33—C32	155.8 (2)	C441—C44—C45—C451	0.8 (8)
S21—Ir1—C33—C32	−18.9 (5)	Ir2—C44—C45—C451	124.0 (5)
S11—Ir1—C33—C32	−98.5 (3)	C43—C44—C45—Ir2	62.3 (3)
C35—Ir1—C33—C331	−160.8 (6)	C441—C44—C45—Ir2	−123.1 (5)
C31—Ir1—C33—C331	156.3 (6)	C44—Ir2—C45—C41	117.3 (4)
C34—Ir1—C33—C331	−122.8 (6)	C42—Ir2—C45—C41	36.9 (3)
C32—Ir1—C33—C331	118.2 (6)	C43—Ir2—C45—C41	79.8 (3)
S22—Ir1—C33—C331	−86.0 (5)	S12—Ir2—C45—C41	−64.5 (3)
S21—Ir1—C33—C331	99.3 (5)	S11—Ir2—C45—C41	−141.5 (3)

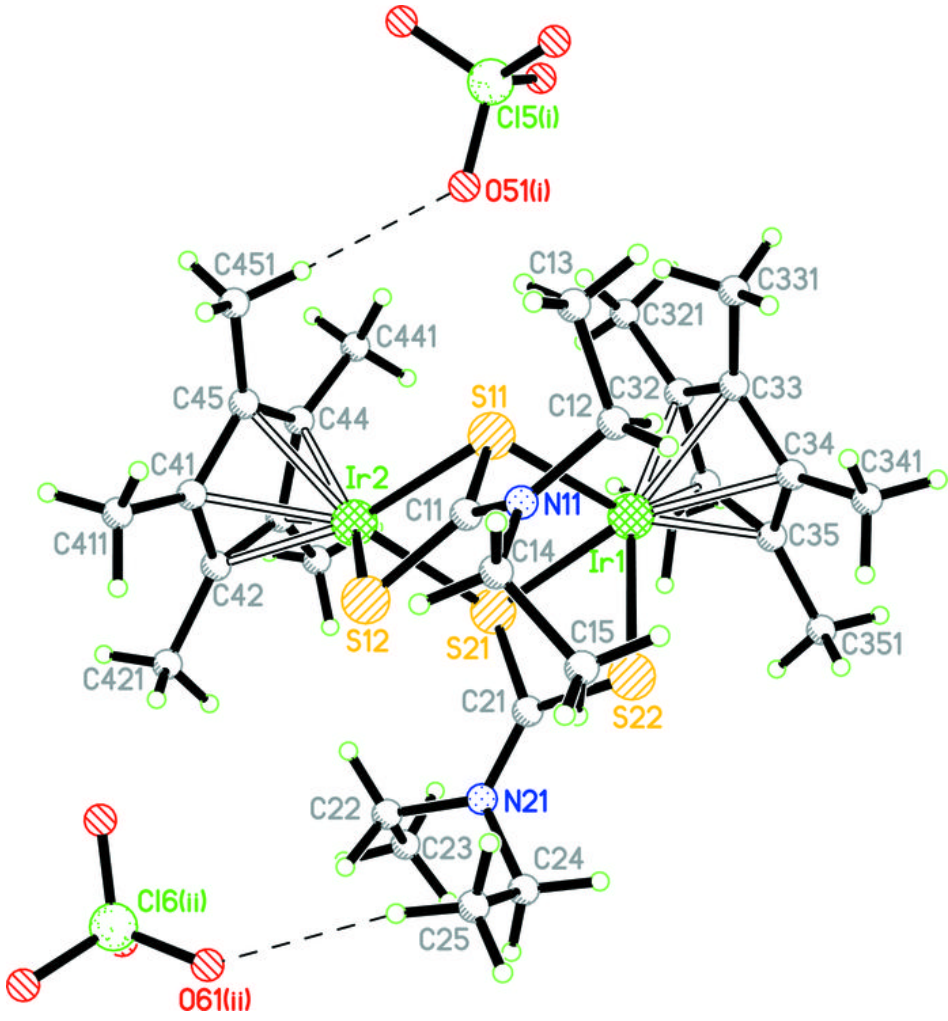
S11—Ir1—C33—C331	19.6 (5)	S21—Ir2—C45—C41	127.2 (3)
C32—C33—C34—C35	0.2 (5)	C41—Ir2—C45—C44	−117.3 (4)
C331—C33—C34—C35	−175.2 (5)	C42—Ir2—C45—C44	−80.4 (3)
Ir1—C33—C34—C35	60.5 (3)	C43—Ir2—C45—C44	−37.4 (3)
C32—C33—C34—C341	177.6 (4)	S12—Ir2—C45—C44	178.3 (2)
C331—C33—C34—C341	2.2 (8)	S11—Ir2—C45—C44	101.2 (3)
Ir1—C33—C34—C341	−122.2 (5)	S21—Ir2—C45—C44	9.9 (4)
C32—C33—C34—Ir1	−60.3 (3)	C41—Ir2—C45—C451	122.1 (6)
C331—C33—C34—Ir1	124.3 (5)	C44—Ir2—C45—C451	−120.7 (5)
C35—Ir1—C34—C33	118.1 (4)	C42—Ir2—C45—C451	158.9 (5)
C31—Ir1—C34—C33	79.9 (3)	C43—Ir2—C45—C451	−158.1 (5)
C32—Ir1—C34—C33	37.2 (3)	S12—Ir2—C45—C451	57.6 (5)
S22—Ir1—C34—C33	−153.3 (3)	S11—Ir2—C45—C451	−19.5 (4)
S21—Ir1—C34—C33	136.1 (3)	S21—Ir2—C45—C451	−110.8 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C451—H452···O51^{i}	0.98	2.41	3.384 (6)	177
C25—H253···O61^{ii}	0.98	2.43	3.398 (7)	168

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

Fig. 1


Cl5(i)
O51(i)
C451
C441
C45
C44
C41
C411
C42
C421
Ir2
S11
S12
S21
C11
N11
C14
Ir1
C15
C21
S22
C13
C321
C331
C32
C33
C12
C34
C341
C35
C351
C22
N21
C23
C24
C25
Cl6(ii)
O61(ii)