# *Appendix C*

## X-RAY DIFFRACTION REPORTS FROM THE BECKMAN INSTITUTE

X-ray structures for compounds **1-Ir(tma)$_2$**, **1b-Ir(tma)$_2$**, **1-Ir(py)$_2$**, **1-Ir(dmap)$_2$**, and **1-Ir(NH$_3$)$_2$** are listed below, along with full reports and analysis, including experimental setup, selected bond lengths, and other relevant parameters. These reports were produced by Michael W. Day at the Beckman Institute. The reports for **1-Ir(tma)$_2$**, **1b-Ir(tma)$_2$**, **1-Ir(py)$_2$**, which were originally PDF files, have been reformatted for the Microsoft Word program, while the reports for **1-Ir(dmap)$_2$**, and **1-Ir(NH$_3$)$_2$**, which were produced in Word format, have largely just been edited in small ways, and therefore appear somewhat different from the former three reports. The nomenclature in all cases has been altered to match that of the thesis.

CALIFORNIA INSTITUTE OF TECHNOLOGY
BECKMAN INSTITUTE
X-RAY CRYSTALLOGRAPHY LABORATORY
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**Crystal Structure Analysis of:**
**1-Ir(tma)$_2$**
(shown below)

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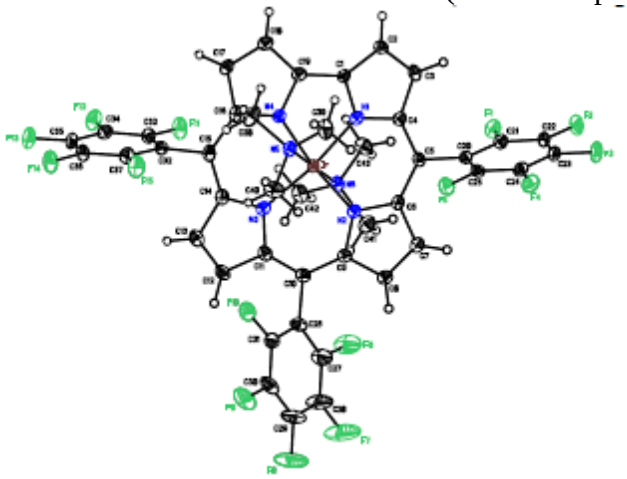

**1-Ir(tma)$_2$**

**Note:** The crystallographic data have been deposited in the Cambridge Database (CCDC) and have been placed on hold pending further instructions from me. The deposition number is 671270. Ideally the CCDC would like the publication to contain a footnote of the type: "Crystallographic data have been deposited at the CCDC, 12 Union Road,

Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 671270".

Table C-1-1. Crystal data and structure refinement for **1-Ir(tma)$_2$** (CCDC 671270)

| | |
|---|---|
| Empirical formula | $C_{43}H_{26}N_6F_{15}Ir \cdot 0.185(CH_2Cl_2)$ |
| Formula weight | 1119.61 |
| Crystallization Solvent | Dichloromethane |
| Crystal Habit | Needle |
| Crystal size | 0.32 x 0.07 x 0.02 mm$^3$ |
| Crystal color | Blue |

## Data Collection

| | | |
|---|---|---|
| Type of diffractometer | Bruker KAPPA APEX II | |
| Wavelength | 0.71073 Å MoKα | |
| Data Collection Temperature | 100(2) K | |
| θ range for 9398 reflections used in lattice determination | 2.54 to 28.61° | |
| Unit cell dimensions | a = 8.1456(4) Å<br>b = 13.1188(6) Å<br>c = 19.8366(8) Å | α= 80.628(3)°<br>β= 80.543(3)°<br>γ = 89.488(3)° |
| Volume | 2062.68(16) Å$^3$ | |
| Z | 2 | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Density (calculated) | 1.803 Mg/m$^3$ | |
| F(000) | 1092 | |
| θ range for data collection | 1.57 to 28.65° | |
| Completeness to θ = 28.65° | 99.2 % | |
| Index ranges | $-10 \le h \le 10$, $-17 \le k \le 17$, $-26 \le l \le 26$ | |
| Data collection scan type | *w* scans; 22 settings | |
| Reflections collected | 70274 | |
| Independent reflections | 10507 [$R_{int}$= 0.0628] | |
| Absorption coefficient | 3.370 mm$^{-1}$ | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7457 and 0.6119 | |

Table C-1-1 (cont.)

**Structure Solution and Refinement**

| | |
|---|---|
| Structure solution program | SHELXS-97 (Sheldrick, 1990) |
| Primary solution method | Direct methods |
| Secondary solution method | Difference Fourier map |
| Hydrogen placement | Geometric positions |
| Structure refinement program | SHELXL-97 (Sheldrick, 1997) |
| Refinement method | Full matrix least-squares on $F^2$ |
| Data / restraints / parameters | 10507 / 0 / 620 |
| Treatment of hydrogen atoms | Riding |
| Goodness-of-fit on $F^2$ | 1.818 |
| Final R indices [$I>2\sigma(I)$, 9104 reflections] | R1 = 0.0330, *w*R2 = 0.0548 |
| R indices (all data) | R1 = 0.0458, *w*R2 = 0.0561 |
| Type of weighting scheme used | Sigma |
| Weighting scheme used | $w=1/\sigma^2(Fo^2)$ |
| Max shift/error | 0.001 |
| Average shift/error | 0.000 |
| Largest diff. peak and hole | 1.996 and -1.834 e.Å$^{-3}$ |

**Special Refinement Details**

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

The crystals contain dichloromethane as a solvent of crystallization. It was refined with partial occupancy in the asymmetric unit with a final refined value of Occ = 0.185.

Refinement of $F^2$ against ALL reflections. The weighted R-factor (*w*R) 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 $F^2 > 2\sigma(F^2)$ 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.

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.

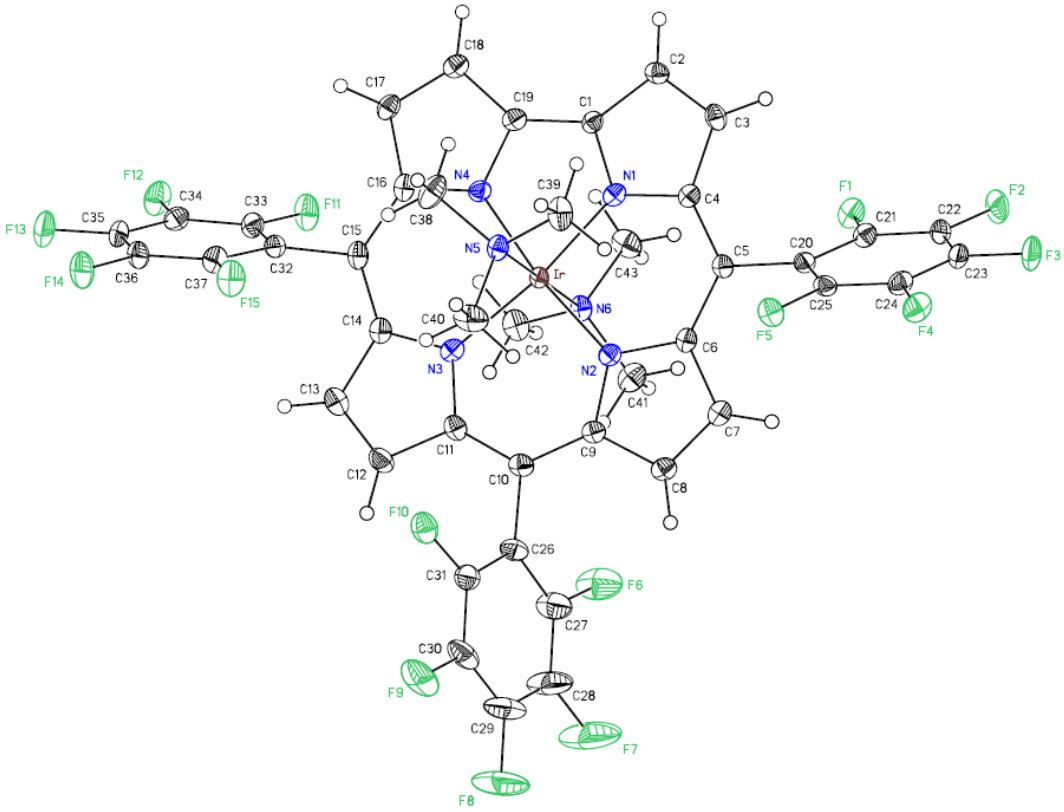

Table C-1-2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for **1-Ir(tma)$_2$** (CCDC 671270). U(eq) is defined as the trace of the orthogonalized Uij tensor.

| | x | y | z | $U_{eq}$ | Occ |
|---|---|---|---|---|---|
| Ir | 1324(1) | 2479(1) | 7024(1) | 12(1) | 1 |
| F(1) | 2573(2) | 6662(2) | 6126(1) | 22(1) | 1 |
| F(2) | 1653(3) | 8597(2) | 5712(1) | 29(1) | 1 |
| F(3) | -1593(3) | 9019(2) | 5636(1) | 30(1) | 1 |
| F(4) | -3922(2) | 7467(2) | 5984(1) | 24(1) | 1 |
| F(5) | -3029(2) | 5525(2) | 6378(1) | 20(1) | 1 |
| F(6) | -857(3) | 3257(2) | 9648(1) | 47(1) | 1 |
| F(7) | -3076(4) | 3111(3) | 10825(1) | 77(1) | 1 |
| F(8) | -5838(4) | 1883(3) | 11010(1) | 68(1) | 1 |
| F(9) | -6354(3) | 799(2) | 10003(1) | 41(1) | 1 |
| F(10) | -4104(2) | 887(2) | 8849(1) | 25(1) | 1 |
| F(11) | 6068(2) | -569(2) | 7429(1) | 26(1) | 1 |
| F(12) | 6967(2) | -2552(2) | 7641(1) | 27(1) | 1 |
| F(13) | 4673(3) | -4087(2) | 7761(1) | 29(1) | 1 |
| F(14) | 1475(3) | -3621(2) | 7630(1) | 28(1) | 1 |
| F(15) | 577(2) | -1642(2) | 7363(1) | 26(1) | 1 |
| N(1) | 2027(3) | 3495(2) | 6203(1) | 14(1) | 1 |
| N(2) | -342(3) | 3405(2) | 7438(1) | 15(1) | 1 |
| N(3) | 807(3) | 1315(2) | 7794(1) | 14(1) | 1 |
| N(4) | 3056(3) | 1707(2) | 6516(1) | 15(1) | 1 |
| N(5) | -560(3) | 1907(2) | 6503(1) | 15(1) | 1 |
| N(6) | 3187(3) | 3064(2) | 7548(1) | 15(1) | 1 |
| C(1) | 3191(4) | 3214(2) | 5691(2) | 14(1) | 1 |
| C(2) | 3443(4) | 4078(3) | 5149(2) | 16(1) | 1 |
| C(3) | 2414(4) | 4851(3) | 5346(2) | 17(1) | 1 |
| C(4) | 1519(4) | 4486(2) | 6029(2) | 14(1) | 1 |
| C(5) | 295(4) | 4921(2) | 6494(2) | 14(1) | 1 |
| C(6) | -536(4) | 4425(3) | 7153(2) | 14(1) | 1 |
| C(7) | -1670(4) | 4855(3) | 7659(2) | 16(1) | 1 |
| C(8) | -2129(4) | 4108(3) | 8221(2) | 17(1) | 1 |
| C(9) | -1263(4) | 3180(3) | 8087(2) | 14(1) | 1 |
| C(10) | -1247(4) | 2211(3) | 8522(2) | 16(1) | 1 |
| C(11) | -262(4) | 1344(3) | 8396(2) | 16(1) | 1 |
| C(12) | -200(4) | 356(3) | 8833(2) | 20(1) | 1 |
| C(13) | 890(4) | -230(3) | 8481(2) | 21(1) | 1 |
| C(14) | 1562(4) | 364(3) | 7815(2) | 16(1) | 1 |
| C(15) | 2758(4) | 78(3) | 7282(2) | 17(1) | 1 |
| C(16) | 3479(4) | 701(3) | 6654(2) | 16(1) | 1 |
| C(17) | 4585(4) | 507(3) | 6045(2) | 17(1) | 1 |
| C(18) | 4750(4) | 1408(3) | 5568(2) | 17(1) | 1 |
| C(19) | 3759(4) | 2178(3) | 5863(2) | 16(1) | 1 |
| C(20) | -188(4) | 6007(2) | 6265(2) | 14(1) | 1 |
| C(21) | 952(4) | 6826(3) | 6082(2) | 17(1) | 1 |
| C(22) | 504(5) | 7828(3) | 5870(2) | 20(1) | 1 |
| C(23) | -1140(5) | 8048(3) | 5836(2) | 20(1) | 1 |
| C(24) | -2305(4) | 7261(3) | 6011(2) | 18(1) | 1 |
| C(25) | -1832(4) | 6264(3) | 6217(2) | 16(1) | 1 |

| | | | | | |
|---|---|---|---|---|---|
| C(26) | -2414(4) | 2103(3) | 9196(2) | 20(1) | 1 |
| C(27) | -2212(5) | 2640(3) | 9724(2) | 31(1) | 1 |
| C(28) | -3327(6) | 2570(4) | 10326(2) | 45(1) | 1 |
| C(29) | -4733(6) | 1952(4) | 10428(2) | 41(1) | 1 |
| C(30) | -4987(5) | 1392(3) | 9917(2) | 28(1) | 1 |
| C(31) | -3829(4) | 1461(3) | 9321(2) | 21(1) | 1 |
| C(32) | 3288(4) | -1025(3) | 7392(2) | 15(1) | 1 |
| C(33) | 4912(4) | -1306(3) | 7460(2) | 18(1) | 1 |
| C(34) | 5384(4) | -2315(3) | 7577(2) | 18(1) | 1 |
| C(35) | 4227(4) | -3099(3) | 7635(2) | 19(1) | 1 |
| C(36) | 2605(4) | -2857(3) | 7570(2) | 19(1) | 1 |
| C(37) | 2171(4) | -1838(3) | 7440(2) | 18(1) | 1 |
| C(38) | 12(5) | 1039(3) | 6131(2) | 26(1) | 1 |
| C(39) | -1127(5) | 2734(3) | 5990(2) | 23(1) | 1 |
| C(40) | -2065(4) | 1530(3) | 7013(2) | 26(1) | 1 |
| C(41) | 2496(4) | 3734(3) | 8061(2) | 22(1) | 1 |
| C(42) | 4013(4) | 2201(3) | 7937(2) | 21(1) | 1 |
| C(43) | 4516(4) | 3688(3) | 7045(2) | 23(1) | 1 |
| | | | | | |
| Cl(1) | 6878(13) | 5635(7) | 9770(5) | 95(4) | 0.185(3) |
| Cl(2) | 9171(10) | 7272(6) | 9083(4) | 71(3) | 0.185(3) |
| C(51) | 8800(40) | 5970(20) | 9329(15) | 58(8) | 0.185(3) |

Table C-1-3. Selected bond lengths [Å] and angles [°] for **1-Ir(tma)$_2$** (CCDC 671270)

| | | | |
|---|---|---|---|
| Ir-N(1) | 1.940(3) | N(1)-Ir-N(4) | 79.57(11) |
| Ir-N(4) | 1.968(3) | N(1)-Ir-N(3) | 172.20(12) |
| Ir-N(3) | 1.970(3) | N(4)-Ir-N(3) | 92.69(11) |
| Ir-N(2) | 1.981(3) | N(1)-Ir-N(2) | 93.09(11) |
| Ir-N(6) | 2.184(3) | N(4)-Ir-N(2) | 172.66(11) |
| Ir-N(5) | 2.186(3) | N(3)-Ir-N(2) | 94.64(11) |
| | | N(1)-Ir-N(6) | 90.92(11) |
| | | N(4)-Ir-N(6) | 89.98(11) |
| | | N(3)-Ir-N(6) | 90.11(10) |
| | | N(2)-Ir-N(6) | 89.78(11) |
| | | N(1)-Ir-N(5) | 89.02(11) |
| | | N(4)-Ir-N(5) | 90.67(11) |
| | | N(3)-Ir-N(5) | 90.04(11) |
| | | N(2)-Ir-N(5) | 89.55(11) |
| | | N(6)-Ir-N(5) | 179.32(12) |

Table C-1-4. Bond lengths [Å] and angles [°] for **1-Ir(tma)$_2$** (CCDC 671270)

| | | | |
|---|---|---|---|
| Ir-N(1) | 1.940(3) | C(14)-C(15) | 1.411(5) |
| Ir-N(4) | 1.968(3) | C(15)-C(16) | 1.415(5) |
| Ir-N(3) | 1.970(3) | C(15)-C(32) | 1.499(5) |
| Ir-N(2) | 1.981(3) | C(16)-C(17) | 1.439(5) |
| Ir-N(6) | 2.184(3) | C(17)-C(18) | 1.381(5) |
| Ir-N(5) | 2.186(3) | C(18)-C(19) | 1.427(5) |
| F(1)-C(21) | 1.351(4) | C(20)-C(21) | 1.389(5) |
| F(2)-C(22) | 1.345(4) | C(20)-C(25) | 1.392(4) |
| F(3)-C(23) | 1.338(4) | C(21)-C(22) | 1.378(5) |
| F(4)-C(24) | 1.350(4) | C(22)-C(23) | 1.378(5) |
| F(5)-C(25) | 1.343(4) | C(23)-C(24) | 1.371(5) |
| F(6)-C(27) | 1.348(5) | C(24)-C(25) | 1.378(5) |
| F(7)-C(28) | 1.349(5) | C(26)-C(27) | 1.386(5) |
| F(8)-C(29) | 1.333(5) | C(26)-C(31) | 1.398(5) |
| F(9)-C(30) | 1.336(5) | C(27)-C(28) | 1.368(6) |
| F(10)-C(31) | 1.340(4) | C(28)-C(29) | 1.378(7) |
| F(11)-C(33) | 1.342(4) | C(29)-C(30) | 1.387(6) |
| F(12)-C(34) | 1.346(4) | C(30)-C(31) | 1.377(5) |
| F(13)-C(35) | 1.338(4) | C(32)-C(37) | 1.389(5) |
| F(14)-C(36) | 1.344(4) | C(32)-C(33) | 1.392(5) |
| F(15)-C(37) | 1.350(4) | C(33)-C(34) | 1.369(5) |
| N(1)-C(1) | 1.366(4) | C(34)-C(35) | 1.379(5) |
| N(1)-C(4) | 1.368(4) | C(35)-C(36) | 1.378(5) |
| N(2)-C(9) | 1.368(4) | C(36)-C(37) | 1.374(5) |
| N(2)-C(6) | 1.383(4) | Cl(1)-C(51) | 1.68(3) |
| N(3)-C(11) | 1.363(4) | Cl(2)-C(51) | 1.72(3) |
| N(3)-C(14) | 1.383(4) | | |
| N(4)-C(16) | 1.357(4) | N(1)-Ir-N(4) | 79.57(11) |
| N(4)-C(19) | 1.375(4) | N(1)-Ir-N(3) | 172.20(12) |
| N(5)-C(40) | 1.487(4) | N(4)-Ir-N(3) | 92.69(11) |
| N(5)-C(38) | 1.487(5) | N(1)-Ir-N(2) | 93.09(11) |
| N(5)-C(39) | 1.487(4) | N(4)-Ir-N(2) | 172.66(11) |
| N(6)-C(42) | 1.483(4) | N(3)-Ir-N(2) | 94.64(11) |
| N(6)-C(41) | 1.489(5) | N(1)-Ir-N(6) | 90.92(11) |
| N(6)-C(43) | 1.495(4) | N(4)-Ir-N(6) | 89.98(11) |
| C(1)-C(2) | 1.420(4) | N(3)-Ir-N(6) | 90.11(10) |
| C(1)-C(19) | 1.437(5) | N(2)-Ir-N(6) | 89.78(11) |
| C(2)-C(3) | 1.375(5) | N(1)-Ir-N(5) | 89.02(11) |
| C(3)-C(4) | 1.438(5) | N(4)-Ir-N(5) | 90.67(11) |
| C(4)-C(5) | 1.424(5) | N(3)-Ir-N(5) | 90.04(11) |
| C(5)-C(6) | 1.425(4) | N(2)-Ir-N(5) | 89.55(11) |
| C(5)-C(20) | 1.493(4) | N(6)-Ir-N(5) | 179.32(12) |
| C(6)-C(7) | 1.431(5) | C(1)-N(1)-C(4) | 111.6(3) |
| C(7)-C(8) | 1.364(5) | C(1)-N(1)-Ir | 118.0(2) |
| C(8)-C(9) | 1.442(5) | C(4)-N(1)-Ir | 130.4(2) |
| C(9)-C(10) | 1.416(4) | C(9)-N(2)-C(6) | 110.8(3) |
| C(10)-C(11) | 1.418(5) | C(9)-N(2)-Ir | 124.6(2) |
| C(10)-C(26) | 1.494(5) | C(6)-N(2)-Ir | 123.9(2) |
| C(11)-C(12) | 1.443(4) | C(11)-N(3)-C(14) | 110.2(3) |
| C(12)-C(13) | 1.352(5) | C(11)-N(3)-Ir | 125.4(2) |
| C(13)-C(14) | 1.444(5) | C(14)-N(3)-Ir | 124.3(2) |

| | | | |
|---|---|---|---|
| C(16)-N(4)-C(19) | 112.7(3) | N(4)-C(19)-C(1) | 112.8(3) |
| C(16)-N(4)-Ir | 129.7(2) | C(18)-C(19)-C(1) | 141.6(3) |
| C(19)-N(4)-Ir | 116.5(2) | C(21)-C(20)-C(25) | 115.4(3) |
| C(40)-N(5)-C(38) | 107.0(3) | C(21)-C(20)-C(5) | 122.9(3) |
| C(40)-N(5)-C(39) | 106.3(3) | C(25)-C(20)-C(5) | 121.7(3) |
| C(38)-N(5)-C(39) | 107.2(3) | F(1)-C(21)-C(22) | 117.1(3) |
| C(40)-N(5)-Ir | 110.4(2) | F(1)-C(21)-C(20) | 120.0(3) |
| C(38)-N(5)-Ir | 113.6(2) | C(22)-C(21)-C(20) | 122.9(3) |
| C(39)-N(5)-Ir | 111.9(2) | F(2)-C(22)-C(23) | 119.7(3) |
| C(42)-N(6)-C(41) | 106.2(3) | F(2)-C(22)-C(21) | 120.5(3) |
| C(42)-N(6)-C(43) | 107.3(3) | C(23)-C(22)-C(21) | 119.8(3) |
| C(41)-N(6)-C(43) | 106.6(3) | F(3)-C(23)-C(24) | 120.5(3) |
| C(42)-N(6)-Ir | 110.9(2) | F(3)-C(23)-C(22) | 120.3(3) |
| C(41)-N(6)-Ir | 113.9(2) | C(24)-C(23)-C(22) | 119.2(3) |
| C(43)-N(6)-Ir | 111.6(2) | F(4)-C(24)-C(23) | 119.8(3) |
| N(1)-C(1)-C(2) | 106.5(3) | F(4)-C(24)-C(25) | 120.0(3) |
| N(1)-C(1)-C(19) | 112.8(3) | C(23)-C(24)-C(25) | 120.2(3) |
| C(2)-C(1)-C(19) | 140.7(3) | F(5)-C(25)-C(24) | 117.4(3) |
| C(3)-C(2)-C(1) | 108.2(3) | F(5)-C(25)-C(20) | 120.0(3) |
| C(2)-C(3)-C(4) | 108.0(3) | C(24)-C(25)-C(20) | 122.6(3) |
| N(1)-C(4)-C(5) | 120.2(3) | C(27)-C(26)-C(31) | 115.6(3) |
| N(1)-C(4)-C(3) | 105.7(3) | C(27)-C(26)-C(10) | 123.4(3) |
| C(5)-C(4)-C(3) | 134.1(3) | C(31)-C(26)-C(10) | 121.0(3) |
| C(4)-C(5)-C(6) | 126.9(3) | F(6)-C(27)-C(28) | 117.9(4) |
| C(4)-C(5)-C(20) | 116.8(3) | F(6)-C(27)-C(26) | 119.1(3) |
| C(6)-C(5)-C(20) | 116.3(3) | C(28)-C(27)-C(26) | 123.0(4) |
| N(2)-C(6)-C(5) | 125.2(3) | F(7)-C(28)-C(27) | 120.7(4) |
| N(2)-C(6)-C(7) | 106.0(3) | F(7)-C(28)-C(29) | 119.2(4) |
| C(5)-C(6)-C(7) | 128.7(3) | C(27)-C(28)-C(29) | 120.1(4) |
| C(8)-C(7)-C(6) | 108.8(3) | F(8)-C(29)-C(28) | 120.9(4) |
| C(7)-C(8)-C(9) | 107.7(3) | F(8)-C(29)-C(30) | 120.0(4) |
| N(2)-C(9)-C(10) | 123.7(3) | C(28)-C(29)-C(30) | 119.2(4) |
| N(2)-C(9)-C(8) | 106.7(3) | F(9)-C(30)-C(31) | 120.5(4) |
| C(10)-C(9)-C(8) | 129.6(3) | F(9)-C(30)-C(29) | 120.0(4) |
| C(9)-C(10)-C(11) | 128.0(3) | C(31)-C(30)-C(29) | 119.5(4) |
| C(9)-C(10)-C(26) | 115.3(3) | F(10)-C(31)-C(30) | 117.5(3) |
| C(11)-C(10)-C(26) | 116.7(3) | F(10)-C(31)-C(26) | 119.9(3) |
| N(3)-C(11)-C(10) | 123.3(3) | C(30)-C(31)-C(26) | 122.6(4) |
| N(3)-C(11)-C(12) | 107.5(3) | C(37)-C(32)-C(33) | 115.6(3) |
| C(10)-C(11)-C(12) | 129.2(3) | C(37)-C(32)-C(15) | 121.7(3) |
| C(13)-C(12)-C(11) | 107.4(3) | C(33)-C(32)-C(15) | 122.7(3) |
| C(12)-C(13)-C(14) | 108.9(3) | F(11)-C(33)-C(34) | 117.8(3) |
| N(3)-C(14)-C(15) | 125.0(3) | F(11)-C(33)-C(32) | 119.6(3) |
| N(3)-C(14)-C(13) | 106.0(3) | C(34)-C(33)-C(32) | 122.6(3) |
| C(15)-C(14)-C(13) | 129.0(3) | F(12)-C(34)-C(33) | 120.6(3) |
| C(14)-C(15)-C(16) | 127.8(3) | F(12)-C(34)-C(35) | 119.4(3) |
| C(14)-C(15)-C(32) | 115.6(3) | C(33)-C(34)-C(35) | 120.0(3) |
| C(16)-C(15)-C(32) | 116.6(3) | F(13)-C(35)-C(36) | 120.3(3) |
| N(4)-C(16)-C(15) | 120.0(3) | F(13)-C(35)-C(34) | 120.3(3) |
| N(4)-C(16)-C(17) | 105.6(3) | C(36)-C(35)-C(34) | 119.5(3) |
| C(15)-C(16)-C(17) | 134.3(3) | F(14)-C(36)-C(37) | 121.1(3) |
| C(18)-C(17)-C(16) | 107.9(3) | F(14)-C(36)-C(35) | 119.5(3) |
| C(17)-C(18)-C(19) | 108.4(3) | C(37)-C(36)-C(35) | 119.4(3) |
| N(4)-C(19)-C(18) | 105.4(3) | F(15)-C(37)-C(36) | 117.1(3) |
| F(15)-C(37)-C(32) | 119.9(3) | Cl(1)-C(51)-Cl(2) | 115.1(16) |
| C(36)-C(37)-C(32) | 122.9(3) | | |

Table C-1-5. Anisotropic displacement parameters ($Å^2$ x $10^4$) for **1-Ir(tma)$_2$** (CCDC 671270). The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [ $h^2 a^{*2} U^{11}$ + … + 2 h k a* b* $U^{12}$ ].

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ir | 84(1) | 112(1) | 151(1) | -24(1) | -12(1) | -12(1) |
| F(1) | 125(11) | 215(11) | 329(12) | -94(9) | -24(9) | -44(8) |
| F(2) | 288(13) | 160(11) | 402(13) | -42(9) | 19(10) | -112(9) |
| F(3) | 410(14) | 118(10) | 357(13) | -29(9) | -72(11) | 63(9) |
| F(4) | 184(11) | 255(11) | 285(12) | -61(9) | -66(9) | 95(9) |
| F(5) | 136(10) | 204(11) | 250(11) | -13(9) | -45(9) | -31(8) |
| F(6) | 426(16) | 668(18) | 344(14) | -232(13) | -7(12) | -238(13) |
| F(7) | 790(20) | 1220(30) | 327(15) | -425(17) | 121(15) | -290(20) |
| F(8) | 552(19) | 1040(30) | 328(15) | -117(16) | 267(14) | -123(17) |
| F(9) | 187(12) | 430(15) | 494(15) | 108(12) | 95(11) | -67(11) |
| F(10) | 196(11) | 218(11) | 311(12) | -6(9) | -33(9) | -39(9) |
| F(11) | 145(11) | 183(11) | 453(14) | -42(10) | -62(10) | -45(9) |
| F(12) | 154(11) | 225(11) | 423(13) | -77(10) | -45(10) | 63(9) |
| F(13) | 290(13) | 137(11) | 448(14) | -61(10) | -51(10) | 37(9) |
| F(14) | 257(12) | 173(11) | 417(13) | -45(10) | -85(10) | -85(9) |
| F(15) | 154(11) | 235(11) | 405(13) | -49(10) | -111(10) | -17(9) |
| N(1) | 89(15) | 161(15) | 172(15) | -51(12) | -29(12) | 12(12) |
| N(2) | 128(15) | 154(15) | 159(15) | -35(12) | -24(12) | 10(12) |
| N(3) | 73(14) | 172(15) | 185(15) | -57(12) | -18(12) | -5(12) |
| N(4) | 122(15) | 155(15) | 160(15) | -36(12) | 0(12) | 7(12) |
| N(5) | 119(15) | 136(15) | 214(16) | -43(12) | -37(13) | -17(12) |
| N(6) | 114(15) | 139(15) | 198(16) | -15(12) | -38(12) | -12(12) |
| C(1) | 124(18) | 136(17) | 165(17) | -48(14) | -16(14) | -16(14) |
| C(2) | 134(18) | 179(18) | 151(17) | -30(14) | -9(14) | -48(14) |
| C(3) | 151(19) | 144(17) | 214(19) | 0(14) | -32(15) | -37(14) |
| C(4) | 105(17) | 147(17) | 169(17) | -47(14) | -34(14) | -18(13) |
| C(5) | 108(17) | 137(16) | 171(18) | -22(14) | -31(14) | -18(13) |
| C(6) | 115(17) | 135(17) | 188(18) | -37(14) | -38(14) | -3(13) |
| C(7) | 119(17) | 170(17) | 199(18) | -56(14) | -51(14) | 9(14) |
| C(8) | 114(18) | 202(19) | 190(18) | -50(15) | -9(14) | -3(14) |
| C(9) | 96(17) | 173(17) | 161(17) | -38(14) | -22(14) | -21(14) |
| C(10) | 117(18) | 198(18) | 174(18) | -33(14) | -10(14) | -38(14) |
| C(11) | 111(17) | 166(18) | 202(18) | -5(14) | -28(14) | -26(14) |
| C(12) | 171(19) | 192(19) | 205(19) | 20(15) | 11(15) | -13(15) |
| C(13) | 190(20) | 183(18) | 225(19) | 13(15) | -42(16) | -21(15) |
| C(14) | 117(18) | 151(17) | 216(19) | -27(14) | -39(15) | -3(14) |
| C(15) | 132(18) | 131(17) | 245(19) | -29(15) | -65(15) | -23(14) |
| C(16) | 125(18) | 128(17) | 237(19) | -37(14) | -64(15) | 5(14) |
| C(17) | 132(18) | 166(18) | 225(19) | -72(15) | -29(15) | 23(14) |
| C(18) | 125(18) | 199(18) | 197(18) | -66(15) | -13(14) | -8(14) |
| C(19) | 103(17) | 183(18) | 180(18) | -54(14) | -1(14) | -34(14) |
| C(20) | 162(18) | 141(17) | 129(17) | -26(13) | -23(14) | -9(14) |
| C(21) | 152(18) | 172(17) | 184(18) | -50(14) | -34(15) | -10(14) |
| C(22) | 260(20) | 129(17) | 191(18) | -47(14) | -3(16) | -61(15) |
| C(23) | 300(20) | 125(17) | 177(18) | -31(14) | -35(16) | 33(15) |
| C(24) | 166(19) | 194(18) | 189(18) | -49(15) | -36(15) | 58(15) |
| C(25) | 148(18) | 170(17) | 143(17) | -30(14) | 1(14) | -39(14) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(26) | 152(19) | 252(19) | 163(18) | -15(15) | 8(15) | -7(15) |
| C(27) | 290(20) | 390(20) | 230(20) | -68(18) | 0(18) | -77(19) |
| C(28) | 500(30) | 670(30) | 190(20) | -170(20) | 30(20) | -70(30) |
| C(29) | 390(30) | 570(30) | 200(20) | -20(20) | 100(20) | -10(20) |
| C(30) | 190(20) | 300(20) | 290(20) | 80(18) | 37(17) | -39(17) |
| C(31) | 210(20) | 204(19) | 199(19) | -7(15) | -19(16) | 54(15) |
| C(32) | 159(18) | 140(17) | 159(17) | -24(14) | -21(14) | -11(14) |
| C(33) | 166(19) | 153(17) | 214(19) | -52(14) | -13(15) | -46(14) |
| C(34) | 140(18) | 200(18) | 200(18) | -48(15) | -10(15) | 33(14) |
| C(35) | 220(20) | 120(17) | 228(19) | -35(14) | -30(16) | 38(14) |
| C(36) | 210(20) | 146(17) | 232(19) | -41(14) | -33(16) | -78(15) |
| C(37) | 130(18) | 190(18) | 239(19) | -47(15) | -40(15) | 12(14) |
| C(38) | 220(20) | 250(20) | 380(20) | -172(18) | -117(18) | 15(16) |
| C(39) | 210(20) | 191(19) | 320(20) | -32(16) | -135(17) | -18(16) |
| C(40) | 160(20) | 380(20) | 250(20) | -63(17) | -10(16) | -108(17) |
| C(41) | 190(20) | 250(20) | 270(20) | -104(16) | -77(16) | -18(16) |
| C(42) | 150(20) | 220(20) | 280(20) | -6(16) | -93(16) | -12(15) |
| C(43) | 163(19) | 270(20) | 240(20) | -18(16) | -47(16) | -91(16) |
| | | | | | | |
| Cl(1) | 1080(80) | 550(50) | 1040(70) | -190(50) | 450(60) | -70(50) |
| Cl(2) | 560(50) | 710(60) | 840(60) | 70(40) | -220(40) | -20(40) |
| C(51) | 600(200) | 500(170) | 700(200) | -430(150) | -200(160) | 20(140) |

CALIFORNIA INSTITUTE OF TECHNOLOGY
BECKMAN INSTITUTE
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Date 24 January 2008

**Crystal Structure Analysis of:**
**1b-Ir(tma)$_2$**
(shown below)

**For** Investigator: Joshua Palmer ext. 6332
Advisor: H. B. Gray ext. 6500
Account Number: HGB.BP-1-BP.AMOCO
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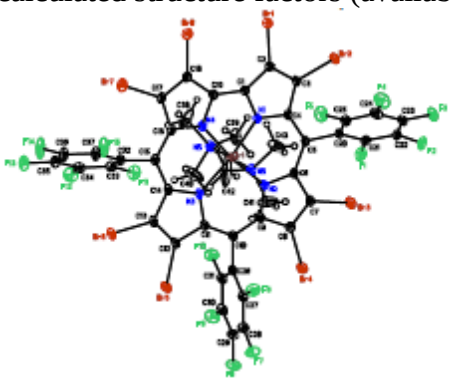

**1b-Ir(tma)$_2$**

**Note:** The crystallographic data have been deposited in the Cambridge Database (CCDC) and have been placed on hold pending further instructions from me. The deposition number is 675602. Ideally the CCDC would like the publication to contain a footnote of the type: "Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 657602".

Table C-2-1. Crystal data and structure refinement for **1b-Ir(tma)$_2$** (CCDC 675602)

| | | |
|---|---|---|
| Empirical formula | $C_{43}H_{18}N_6Br_8F_{17}Ir$, $3(CH_2Cl_2)$ | |
| Formula weight | 1989.89 | |
| Crystallization Solvent | Dichloromethane | |
| Crystal Habit | Block | |
| Crystal size | 0.46 x 0.25 x 0.14 $mm^3$ | |
| Crystal color | Dark green | |
| **Data Collection** | | |
| Type of diffractometer | Bruker KAPPA APEX II | |
| Wavelength | 0.71073 Å MoKα | |
| Data Collection Temperature | 100(2) K | |
| θ range for 9503 reflections used in lattice determination | 2.58 to 43.28° | |
| Unit cell dimensions | a = 10.5456(5) Å<br>b = 12.9293(6) Å<br>c = 21.2776(9) Å | α= 81.591(3)°<br>β= 76.344(3)°<br>γ = 86.714(3)° |
| Volume | 2788.0(2) $Å^3$ | |
| Z | 2 | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Density (calculated) | 2.370 $Mg/m^3$ | |
| F(000) | 1872 | |
| θ range for data collection | 1.76 to 43.48° | |
| Completeness to θ = 43.48° | 96.6 % | |
| Index ranges | $-20 \leq h \leq 20$, $-24 \leq k \leq 22$, $-41 \leq l \leq 40$ | |
| Data collection scan type | ω scans; 24 settings | |
| Reflections collected | 177276 | |
| Independent reflections | 40945 [$R_{int}$= 0.0501] | |
| Absorption coefficient | 8.508 $mm^{-1}$ | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7485 and 0.4771 | |

Table C-2-1 (cont.)

**Structure Solution and Refinement**

| | |
|---|---|
| Structure solution program | SHELXS-97 (Sheldrick, 1990) |
| Primary solution method | Direct methods |
| Secondary solution method | Difference Fourier map |
| Hydrogen placement | Geometric positions |
| Structure refinement program | SHELXL-97 (Sheldrick, 1997) |
| Refinement method | Full matrix least-squares on $F^2$ |
| Data / restraints / parameters | 40945 / 0 / 764 |
| Treatment of hydrogen atoms | Riding |
| Goodness-of-fit on $F^2$ | 1.534 |
| Final R indices [$I>2\sigma(I)$, 28576 reflections] | R1 = 0.0412, *w*R2 = 0.0606 |
| R indices (all data) | R1 = 0.0793, *w*R2 = 0.0634 |
| Type of weighting scheme used | Sigma |
| Weighting scheme used | $w=1/\sigma^2(Fo^2)$ |
| Max shift/error | 0.004 |
| Average shift/error | 0.000 |
| Largest diff. peak and hole | 4.350 and -2.801 e.Å$^{-3}$ |

**Special Refinement Details**

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

The crystals contain dichloromethane as a solvent of crystallization—three in the asymmetric unit. One of those three is disordered with the chlorine atoms occupying two orientations while sharing a common carbon atom. The disorder was modeled without restraint, except that the total chlorine population was restrained so that the orientations' occupancy summed to one.

Refinement of $F^2$ against ALL reflections. The weighted R-factor (*w*R) 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 $F^2 > 2\sigma(F^2)$ 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.

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.

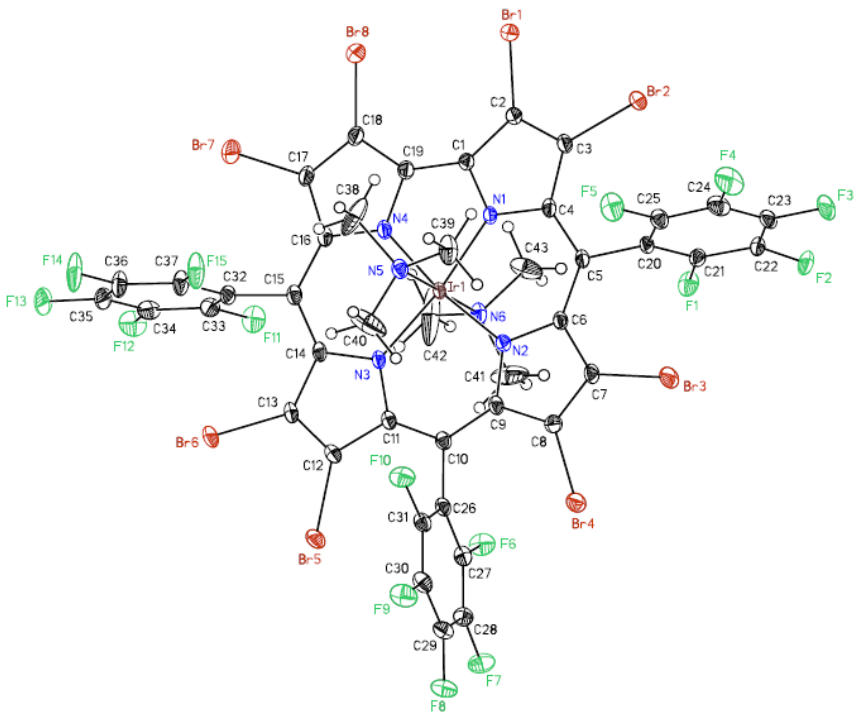

Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for **1b-Ir(tma)$_2$** (CCDC 675602). U(eq) is defined as the trace of the orthogonalized Uij tensor.

| | x | y | z | $U_{eq}$ | Occ |
|---|---|---|---|---|---|
| Ir(1) | 5600(1) | 2707(1) | 2759(1) | 11(1) | 1 |
| Br(1) | 3909(1) | 1493(1) | 5558(1) | 21(1) | 1 |
| Br(2) | 2518(1) | -307(1) | 4875(1) | 21(1) | 1 |
| Br(3) | 2815(1) | -505(1) | 1893(1) | 24(1) | 1 |
| Br(4) | 4474(1) | 911(1) | 528(1) | 20(1) | 1 |
| Br(5) | 8185(1) | 4625(1) | 73(1) | 19(1) | 1 |
| Br(6) | 8884(1) | 6129(1) | 1101(1) | 20(1) | 1 |
| Br(7) | 7691(1) | 5625(1) | 4165(1) | 25(1) | 1 |
| Br(8) | 5967(1) | 3715(1) | 5284(1) | 21(1) | 1 |
| F(1) | 4745(1) | -1423(1) | 3164(1) | 23(1) | 1 |
| F(2) | 3299(1) | -3156(1) | 3442(1) | 27(1) | 1 |
| F(3) | 664(1) | -2985(1) | 3816(1) | 31(1) | 1 |
| F(4) | -531(1) | -1066(1) | 3821(1) | 33(1) | 1 |
| F(5) | 909(1) | 668(1) | 3487(1) | 28(1) | 1 |
| F(6) | 8099(1) | 1767(1) | 282(1) | 23(1) | 1 |
| F(7) | 8270(1) | 1915(1) | -1015(1) | 24(1) | 1 |
| F(8) | 6419(1) | 3027(1) | -1548(1) | 25(1) | 1 |
| F(9) | 4470(1) | 4040(1) | -792(1) | 26(1) | 1 |
| F(10) | 4310(1) | 3925(1) | 500(1) | 22(1) | 1 |
| F(11) | 10087(1) | 4930(1) | 2599(1) | 25(1) | 1 |
| F(12) | 11309(1) | 6752(1) | 2474(1) | 29(1) | 1 |
| F(13) | 9936(1) | 8587(1) | 2426(1) | 31(1) | 1 |
| F(14) | 7336(1) | 8600(1) | 2531(1) | 42(1) | 1 |
| F(15) | 6107(1) | 6777(1) | 2626(1) | 33(1) | 1 |
| N(1) | 4654(2) | 1931(1) | 3581(1) | 13(1) | 1 |
| N(2) | 4941(2) | 1826(1) | 2219(1) | 14(1) | 1 |
| N(3) | 6639(1) | 3618(1) | 2001(1) | 13(1) | 1 |
| N(4) | 6125(2) | 3447(1) | 3397(1) | 14(1) | 1 |
| N(5) | 3890(2) | 3752(1) | 2756(1) | 16(1) | 1 |
| N(6) | 7308(2) | 1662(1) | 2749(1) | 17(1) | 1 |
| C(1) | 4824(2) | 2224(1) | 4151(1) | 14(1) | 1 |
| C(2) | 4113(2) | 1495(1) | 4663(1) | 15(1) | 1 |
| C(3) | 3560(2) | 784(1) | 4385(1) | 15(1) | 1 |
| C(4) | 3926(2) | 1065(1) | 3685(1) | 13(1) | 1 |
| C(5) | 3677(2) | 624(1) | 3152(1) | 13(1) | 1 |
| C(6) | 4142(2) | 987(1) | 2479(1) | 14(1) | 1 |
| C(7) | 3882(2) | 585(1) | 1915(1) | 16(1) | 1 |
| C(8) | 4529(2) | 1174(1) | 1364(1) | 15(1) | 1 |
| C(9) | 5232(2) | 1975(1) | 1547(1) | 14(1) | 1 |
| C(10) | 6058(2) | 2754(1) | 1153(1) | 14(1) | 1 |
| C(11) | 6738(2) | 3512(1) | 1358(1) | 13(1) | 1 |
| C(12) | 7557(2) | 4341(1) | 979(1) | 14(1) | 1 |
| C(13) | 7880(2) | 4931(1) | 1397(1) | 14(1) | 1 |
| C(14) | 7305(2) | 4479(1) | 2058(1) | 13(1) | 1 |
| C(15) | 7380(2) | 4814(1) | 2654(1) | 15(1) | 1 |
| C(16) | 6835(2) | 4323(1) | 3292(1) | 15(1) | 1 |
| C(17) | 6849(2) | 4550(1) | 3935(1) | 16(1) | 1 |

| | | | | | |
|---|---|---|---|---|---|
| C(18) | 6142(2) | 3799(1) | 4387(1) | 16(1) | 1 |
| C(19) | 5653(2) | 3094(1) | 4043(1) | 15(1) | 1 |
| C(20) | 2869(2) | -329(1) | 3331(1) | 13(1) | 1 |
| C(21) | 3447(2) | -1321(1) | 3334(1) | 15(1) | 1 |
| C(22) | 2711(2) | -2209(1) | 3483(1) | 18(1) | 1 |
| C(23) | 1378(2) | -2127(2) | 3662(1) | 21(1) | 1 |
| C(24) | 771(2) | -1146(2) | 3665(1) | 22(1) | 1 |
| C(25) | 1523(2) | -275(2) | 3496(1) | 17(1) | 1 |
| C(26) | 6188(2) | 2829(1) | 433(1) | 14(1) | 1 |
| C(27) | 7183(2) | 2327(1) | 28(1) | 16(1) | 1 |
| C(28) | 7280(2) | 2390(2) | -635(1) | 17(1) | 1 |
| C(29) | 6358(2) | 2968(2) | -911(1) | 18(1) | 1 |
| C(30) | 5365(2) | 3485(2) | -520(1) | 18(1) | 1 |
| C(31) | 5296(2) | 3414(1) | 136(1) | 16(1) | 1 |
| C(32) | 8063(2) | 5808(1) | 2612(1) | 15(1) | 1 |
| C(33) | 9384(2) | 5832(2) | 2583(1) | 17(1) | 1 |
| C(34) | 10026(2) | 6748(2) | 2517(1) | 20(1) | 1 |
| C(35) | 9323(2) | 7686(2) | 2494(1) | 22(1) | 1 |
| C(36) | 8009(2) | 7688(2) | 2544(1) | 24(1) | 1 |
| C(37) | 7387(2) | 6761(2) | 2597(1) | 20(1) | 1 |
| C(38) | 3731(2) | 4500(2) | 3240(2) | 39(1) | 1 |
| C(39) | 2666(2) | 3168(2) | 2920(1) | 25(1) | 1 |
| C(40) | 3956(3) | 4381(2) | 2113(1) | 47(1) | 1 |
| C(41) | 7656(3) | 1137(2) | 2154(1) | 41(1) | 1 |
| C(42) | 8466(3) | 2229(2) | 2770(2) | 72(1) | 1 |
| C(43) | 7110(2) | 815(2) | 3308(1) | 32(1) | 1 |
| | | | | | |
| C(51) | 2473(3) | 626(2) | 9260(1) | 36(1) | 1 |
| Cl(1) | 926(1) | 936(1) | 9104(1) | 40(1) | 1 |
| Cl(2) | 3616(1) | 1580(1) | 8896(1) | 57(1) | 1 |
| | | | | | |
| C(52) | 1202(4) | 2774(2) | 707(1) | 53(1) | 1 |
| Cl(3) | 1075(1) | 3496(1) | 1378(1) | 50(1) | 1 |
| Cl(4) | 773(1) | 1482(1) | 931(1) | 58(1) | 1 |
| | | | | | |
| C(53) | 10193(4) | 6577(2) | 5492(2) | 53(1) | 1 |
| Cl(5A) | 9121(2) | 5785(1) | 5443(1) | 54(1) | 0.526(2) |
| Cl(6A) | 9884(2) | 7892(1) | 5425(1) | 55(1) | 0.526(2) |
| Cl(5B) | 8684(1) | 7181(1) | 5220(1) | 41(1) | 0.474(2) |
| Cl(6B) | 10756(2) | 7409(1) | 5851(1) | 54(1) | 0.474(2) |

Table C-2-3. Selected bond lengths [Å] and angles [°] for **1b-Ir(tma)$_2$** (CCDC 675602)

| | | | |
|---|---|---|---|
| Ir(1)-N(1) | 1.9585(16) | N(1)-Ir(1)-N(4) | 79.08(6) |
| Ir(1)-N(4) | 1.9630(14) | N(1)-Ir(1)-N(3) | 172.15(6) |
| Ir(1)-N(3) | 1.9870(15) | N(4)-Ir(1)-N(3) | 93.08(6) |
| Ir(1)-N(2) | 1.9893(14) | N(1)-Ir(1)-N(2) | 93.07(6) |
| Ir(1)-N(6) | 2.1865(15) | N(4)-Ir(1)-N(2) | 172.13(6) |
| Ir(1)-N(5) | 2.1918(14) | N(3)-Ir(1)-N(2) | 94.77(6) |
| | | N(1)-Ir(1)-N(6) | 91.33(6) |
| | | N(4)-Ir(1)-N(6) | 89.55(6) |
| | | N(3)-Ir(1)-N(6) | 88.99(6) |
| | | N(2)-Ir(1)-N(6) | 90.10(6) |
| | | N(1)-Ir(1)-N(5) | 89.15(6) |
| | | N(4)-Ir(1)-N(5) | 91.07(6) |
| | | N(3)-Ir(1)-N(5) | 90.61(6) |
| | | N(2)-Ir(1)-N(5) | 89.33(6) |
| | | N(6)-Ir(1)-N(5) | 179.27(6) |

Table C-2-4. Bond lengths [Å] and angles [°] for **1b-Ir(tma)$_2$** (CCDC 675602)

| | | | |
|---|---|---|---|
| Ir(1)-N(1) | 1.9585(16) | C(7)-C(8) | 1.358(3) |
| Ir(1)-N(4) | 1.9630(14) | C(8)-C(9) | 1.456(2) |
| Ir(1)-N(3) | 1.9870(15) | C(9)-C(10) | 1.409(3) |
| Ir(1)-N(2) | 1.9893(14) | C(10)-C(11) | 1.421(2) |
| Ir(1)-N(6) | 2.1865(15) | C(10)-C(26) | 1.495(2) |
| Ir(1)-N(5) | 2.1918(14) | C(11)-C(12) | 1.439(3) |
| Br(1)-C(2) | 1.8634(17) | C(12)-C(13) | 1.363(2) |
| Br(2)-C(3) | 1.8684(19) | C(13)-C(14) | 1.445(3) |
| Br(3)-C(7) | 1.8656(18) | C(14)-C(15) | 1.419(2) |
| Br(4)-C(8) | 1.8733(16) | C(15)-C(16) | 1.414(3) |
| Br(5)-C(12) | 1.8721(17) | C(15)-C(32) | 1.490(3) |
| Br(6)-C(13) | 1.8726(19) | C(16)-C(17) | 1.444(2) |
| Br(7)-C(17) | 1.8717(18) | C(17)-C(18) | 1.377(3) |
| Br(8)-C(18) | 1.8603(18) | C(18)-C(19) | 1.436(2) |
| F(1)-C(21) | 1.335(2) | C(20)-C(25) | 1.379(3) |
| F(2)-C(22) | 1.345(2) | C(20)-C(21) | 1.388(2) |
| F(3)-C(23) | 1.333(2) | C(21)-C(22) | 1.378(3) |
| F(4)-C(24) | 1.335(2) | C(22)-C(23) | 1.369(3) |
| F(5)-C(25) | 1.347(2) | C(23)-C(24) | 1.387(3) |
| F(6)-C(27) | 1.343(2) | C(24)-C(25) | 1.371(3) |
| F(7)-C(28) | 1.3392(19) | C(26)-C(31) | 1.384(2) |
| F(8)-C(29) | 1.332(2) | C(26)-C(27) | 1.387(2) |
| F(9)-C(30) | 1.341(2) | C(27)-C(28) | 1.380(2) |
| F(10)-C(31) | 1.3449(19) | C(28)-C(29) | 1.381(3) |
| F(11)-C(33) | 1.346(2) | C(29)-C(30) | 1.381(2) |
| F(12)-C(34) | 1.335(2) | C(30)-C(31) | 1.372(2) |
| F(13)-C(35) | 1.337(2) | C(32)-C(33) | 1.382(3) |
| F(14)-C(36) | 1.341(2) | C(32)-C(37) | 1.389(2) |
| F(15)-C(37) | 1.336(2) | C(33)-C(34) | 1.372(3) |
| N(1)-C(4) | 1.357(2) | C(34)-C(35) | 1.385(3) |
| N(1)-C(1) | 1.375(2) | C(35)-C(36) | 1.364(3) |
| N(2)-C(9) | 1.375(2) | C(36)-C(37) | 1.376(3) |
| N(2)-C(6) | 1.378(2) | C(51)-Cl(2) | 1.739(3) |
| N(3)-C(11) | 1.373(2) | C(51)-Cl(1) | 1.753(2) |
| N(3)-C(14) | 1.384(2) | C(52)-Cl(4) | 1.725(3) |
| N(4)-C(16) | 1.356(2) | C(52)-Cl(3) | 1.793(3) |
| N(4)-C(19) | 1.367(2) | C(53)-Cl(5A) | 1.599(4) |
| N(5)-C(40) | 1.475(3) | C(53)-Cl(6B) | 1.618(4) |
| N(5)-C(39) | 1.476(3) | C(53)-Cl(6A) | 1.704(3) |
| N(5)-C(38) | 1.488(2) | C(53)-Cl(5B) | 1.907(4) |
| N(6)-C(42) | 1.472(3) | | |
| N(6)-C(43) | 1.478(3) | N(1)-Ir(1)-N(4) | 79.08(6) |
| N(6)-C(41) | 1.484(2) | N(1)-Ir(1)-N(3) | 172.15(6) |
| C(1)-C(19) | 1.423(3) | N(4)-Ir(1)-N(3) | 93.08(6) |
| C(1)-C(2) | 1.426(3) | N(1)-Ir(1)-N(2) | 93.07(6) |
| C(2)-C(3) | 1.386(2) | N(4)-Ir(1)-N(2) | 172.13(6) |
| C(3)-C(4) | 1.445(2) | N(3)-Ir(1)-N(2) | 94.77(6) |
| C(4)-C(5) | 1.423(2) | N(1)-Ir(1)-N(6) | 91.33(6) |
| C(5)-C(6) | 1.419(2) | N(4)-Ir(1)-N(6) | 89.55(6) |
| C(5)-C(20) | 1.490(3) | N(3)-Ir(1)-N(6) | 88.99(6) |
| C(6)-C(7) | 1.461(2) | N(2)-Ir(1)-N(6) | 90.10(6) |

| | | | |
|---|---|---|---|
| N(1)-Ir(1)-N(5) | 89.15(6) | N(2)-C(9)-C(8) | 105.35(16) |
| N(4)-Ir(1)-N(5) | 91.07(6) | C(10)-C(9)-C(8) | 130.06(15) |
| N(3)-Ir(1)-N(5) | 90.61(6) | C(9)-C(10)-C(11) | 127.82(15) |
| N(2)-Ir(1)-N(5) | 89.33(6) | C(9)-C(10)-C(26) | 116.35(15) |
| N(6)-Ir(1)-N(5) | 179.27(6) | C(11)-C(10)-C(26) | 115.76(16) |
| C(4)-N(1)-C(1) | 112.63(15) | N(3)-C(11)-C(10) | 123.67(16) |
| C(4)-N(1)-Ir(1) | 129.68(11) | N(3)-C(11)-C(12) | 106.17(14) |
| C(1)-N(1)-Ir(1) | 117.38(12) | C(10)-C(11)-C(12) | 130.03(15) |
| C(9)-N(2)-C(6) | 112.37(14) | C(13)-C(12)-C(11) | 108.37(15) |
| C(9)-N(2)-Ir(1) | 124.19(13) | C(13)-C(12)-Br(5) | 122.03(15) |
| C(6)-N(2)-Ir(1) | 123.44(11) | C(11)-C(12)-Br(5) | 129.58(13) |
| C(11)-N(3)-C(14) | 111.38(15) | C(12)-C(13)-C(14) | 108.59(16) |
| C(11)-N(3)-Ir(1) | 124.90(12) | C(12)-C(13)-Br(6) | 122.26(14) |
| C(14)-N(3)-Ir(1) | 123.64(11) | C(14)-C(13)-Br(6) | 129.15(13) |
| C(16)-N(4)-C(19) | 113.34(14) | N(3)-C(14)-C(15) | 125.53(17) |
| C(16)-N(4)-Ir(1) | 129.08(13) | N(3)-C(14)-C(13) | 105.44(14) |
| C(19)-N(4)-Ir(1) | 117.42(12) | C(15)-C(14)-C(13) | 129.03(17) |
| C(40)-N(5)-C(39) | 106.81(19) | C(16)-C(15)-C(14) | 126.93(17) |
| C(40)-N(5)-C(38) | 106.9(2) | C(16)-C(15)-C(32) | 115.67(15) |
| C(39)-N(5)-C(38) | 106.20(17) | C(14)-C(15)-C(32) | 117.36(16) |
| C(40)-N(5)-Ir(1) | 112.08(12) | N(4)-C(16)-C(15) | 121.45(15) |
| C(39)-N(5)-Ir(1) | 111.87(11) | N(4)-C(16)-C(17) | 105.17(16) |
| C(38)-N(5)-Ir(1) | 112.58(12) | C(15)-C(16)-C(17) | 133.39(17) |
| C(42)-N(6)-C(43) | 106.8(2) | C(18)-C(17)-C(16) | 108.05(15) |
| C(42)-N(6)-C(41) | 107.0(2) | C(18)-C(17)-Br(7) | 123.09(13) |
| C(43)-N(6)-C(41) | 106.00(17) | C(16)-C(17)-Br(7) | 128.83(15) |
| C(42)-N(6)-Ir(1) | 111.72(12) | C(17)-C(18)-C(19) | 108.27(15) |
| C(43)-N(6)-Ir(1) | 112.88(12) | C(17)-C(18)-Br(8) | 123.95(13) |
| C(41)-N(6)-Ir(1) | 112.03(12) | C(19)-C(18)-Br(8) | 127.70(15) |
| N(1)-C(1)-C(19) | 112.90(16) | N(4)-C(19)-C(1) | 113.19(15) |
| N(1)-C(1)-C(2) | 105.70(15) | N(4)-C(19)-C(18) | 105.14(16) |
| C(19)-C(1)-C(2) | 141.36(16) | C(1)-C(19)-C(18) | 141.56(17) |
| C(3)-C(2)-C(1) | 108.27(15) | C(25)-C(20)-C(21) | 116.82(17) |
| C(3)-C(2)-Br(1) | 124.84(15) | C(25)-C(20)-C(5) | 122.19(15) |
| C(1)-C(2)-Br(1) | 126.89(13) | C(21)-C(20)-C(5) | 120.99(16) |
| C(2)-C(3)-C(4) | 107.76(16) | F(1)-C(21)-C(22) | 118.77(16) |
| C(2)-C(3)-Br(2) | 123.21(13) | F(1)-C(21)-C(20) | 119.55(17) |
| C(4)-C(3)-Br(2) | 129.02(13) | C(22)-C(21)-C(20) | 121.63(17) |
| N(1)-C(4)-C(5) | 120.88(16) | F(2)-C(22)-C(23) | 119.87(18) |
| N(1)-C(4)-C(3) | 105.61(14) | F(2)-C(22)-C(21) | 120.17(18) |
| C(5)-C(4)-C(3) | 133.51(17) | C(23)-C(22)-C(21) | 119.94(17) |
| C(6)-C(5)-C(4) | 126.60(17) | F(3)-C(23)-C(22) | 120.14(18) |
| C(6)-C(5)-C(20) | 117.69(15) | F(3)-C(23)-C(24) | 120.06(19) |
| C(4)-C(5)-C(20) | 115.70(15) | C(22)-C(23)-C(24) | 119.78(18) |
| N(2)-C(6)-C(5) | 126.18(15) | F(4)-C(24)-C(25) | 121.18(18) |
| N(2)-C(6)-C(7) | 105.08(15) | F(4)-C(24)-C(23) | 119.73(19) |
| C(5)-C(6)-C(7) | 128.74(17) | C(25)-C(24)-C(23) | 119.08(18) |
| C(8)-C(7)-C(6) | 108.54(16) | F(5)-C(25)-C(24) | 117.90(17) |
| C(8)-C(7)-Br(3) | 122.16(13) | F(5)-C(25)-C(20) | 119.40(17) |
| C(6)-C(7)-Br(3) | 129.26(14) | C(24)-C(25)-C(20) | 122.69(17) |
| C(7)-C(8)-C(9) | 108.64(15) | C(31)-C(26)-C(27) | 116.39(16) |
| C(7)-C(8)-Br(4) | 122.43(14) | C(31)-C(26)-C(10) | 120.65(15) |
| C(9)-C(8)-Br(4) | 128.92(14) | C(27)-C(26)-C(10) | 122.96(15) |
| N(2)-C(9)-C(10) | 124.59(15) | F(6)-C(27)-C(28) | 118.20(15) |

| | | | |
|---|---|---|---|
| F(6)-C(27)-C(26) | 119.42(15) | F(12)-C(34)-C(33) | 121.32(17) |
| C(28)-C(27)-C(26) | 122.38(16) | F(12)-C(34)-C(35) | 119.68(18) |
| F(7)-C(28)-C(27) | 120.86(16) | C(33)-C(34)-C(35) | 119.00(18) |
| F(7)-C(28)-C(29) | 119.62(16) | F(13)-C(35)-C(36) | 120.29(18) |
| C(27)-C(28)-C(29) | 119.51(16) | F(13)-C(35)-C(34) | 119.72(19) |
| F(8)-C(29)-C(28) | 120.62(16) | C(36)-C(35)-C(34) | 119.99(19) |
| F(8)-C(29)-C(30) | 120.02(16) | F(14)-C(36)-C(35) | 119.39(19) |
| C(28)-C(29)-C(30) | 119.36(16) | F(14)-C(36)-C(37) | 120.47(19) |
| F(9)-C(30)-C(31) | 121.11(16) | C(35)-C(36)-C(37) | 120.13(18) |
| F(9)-C(30)-C(29) | 118.98(16) | F(15)-C(37)-C(36) | 119.48(16) |
| C(31)-C(30)-C(29) | 119.90(16) | F(15)-C(37)-C(32) | 119.03(17) |
| F(10)-C(31)-C(30) | 117.99(15) | C(36)-C(37)-C(32) | 121.48(18) |
| F(10)-C(31)-C(26) | 119.55(15) | Cl(2)-C(51)-Cl(1) | 113.23(14) |
| C(30)-C(31)-C(26) | 122.45(16) | Cl(4)-C(52)-Cl(3) | 114.43(17) |
| C(33)-C(32)-C(37) | 116.86(17) | Cl(5A)-C(53)-Cl(6B) | 153.0(2) |
| C(33)-C(32)-C(15) | 122.33(16) | Cl(5A)-C(53)-Cl(6A) | 121.1(2) |
| C(37)-C(32)-C(15) | 120.81(16) | Cl(6B)-C(53)-Cl(6A) | 53.20(12) |
| F(11)-C(33)-C(34) | 118.05(17) | Cl(5A)-C(53)-Cl(5B) | 63.30(15) |
| F(11)-C(33)-C(32) | 119.44(17) | Cl(6B)-C(53)-Cl(5B) | 108.72(16) |
| C(34)-C(33)-C(32) | 122.48(17) | Cl(6A)-C(53)-Cl(5B) | 58.54(12) |

Table C-2-5. Anisotropic displacement parameters ($Å^2$ x $10^4$) for **1b-Ir(tma)$_2$** (CCDC 675602). The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [ $h^2$ $a^{*2}U^{11}$ + … + 2 h k a* b* $U^{12}$ ].

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ir(1) | 107(1) | 77(1) | 142(1) | -10(1) | -5(1) | -15(1) |
| Br(1) | 276(1) | 182(1) | 147(1) | -38(1) | 18(1) | -67(1) |
| Br(2) | 254(1) | 174(1) | 170(1) | -11(1) | 22(1) | -93(1) |
| Br(3) | 279(1) | 253(1) | 190(1) | -6(1) | -46(1) | -175(1) |
| Br(4) | 212(1) | 223(1) | 160(1) | -10(1) | -49(1) | -91(1) |
| Br(5) | 169(1) | 202(1) | 168(1) | 8(1) | 4(1) | -76(1) |
| Br(6) | 212(1) | 155(1) | 208(1) | 17(1) | -16(1) | -93(1) |
| Br(7) | 262(1) | 216(1) | 281(1) | -65(1) | -47(1) | -90(1) |
| Br(8) | 251(1) | 195(1) | 177(1) | -45(1) | -37(1) | -44(1) |
| F(1) | 154(5) | 187(6) | 337(6) | -80(5) | -16(5) | 28(5) |
| F(2) | 429(8) | 105(5) | 273(6) | -58(5) | -81(6) | -2(5) |
| F(3) | 395(8) | 264(7) | 271(6) | 11(5) | -39(6) | -252(6) |
| F(4) | 129(6) | 456(8) | 385(7) | -15(6) | -2(5) | -118(5) |
| F(5) | 172(6) | 221(6) | 404(7) | -18(5) | -27(5) | 56(5) |
| F(6) | 182(6) | 279(7) | 237(6) | -47(5) | -62(5) | 89(5) |
| F(7) | 168(6) | 330(7) | 220(5) | -92(5) | -4(4) | 55(5) |
| F(8) | 256(6) | 321(7) | 135(5) | 4(5) | -19(4) | 4(5) |
| F(9) | 243(7) | 295(7) | 223(6) | 25(5) | -87(5) | 94(5) |
| F(10) | 166(6) | 262(6) | 209(5) | -33(5) | -12(4) | 89(5) |
| F(11) | 170(6) | 234(6) | 355(7) | -48(5) | -83(5) | 51(5) |
| F(12) | 122(5) | 433(8) | 319(6) | -62(6) | -43(5) | -108(5) |
| F(13) | 299(7) | 249(7) | 388(7) | -80(6) | -8(6) | -194(5) |
| F(14) | 266(7) | 110(6) | 821(11) | -118(7) | 11(7) | -20(5) |
| F(15) | 110(5) | 137(6) | 690(10) | -72(6) | -6(6) | -14(4) |
| N(1) | 141(7) | 89(6) | 150(6) | -11(5) | -20(5) | -20(5) |
| N(2) | 142(7) | 113(7) | 143(6) | -15(5) | 3(5) | -28(5) |
| N(3) | 107(6) | 88(6) | 165(6) | -14(5) | 0(5) | -23(5) |
| N(4) | 145(7) | 103(7) | 171(6) | -10(5) | -22(5) | -31(5) |
| N(5) | 138(7) | 118(7) | 189(7) | -11(5) | -2(5) | 7(5) |
| N(6) | 146(7) | 112(7) | 227(7) | -11(6) | -28(6) | -3(6) |
| C(1) | 150(8) | 109(8) | 147(7) | -21(6) | -4(6) | -4(6) |
| C(2) | 172(8) | 124(8) | 148(7) | -19(6) | 1(6) | -14(6) |
| C(3) | 140(8) | 107(8) | 180(8) | -8(6) | 6(6) | -16(6) |
| C(4) | 116(7) | 86(7) | 185(7) | -16(6) | -9(6) | -3(6) |
| C(5) | 110(7) | 88(7) | 179(7) | -15(6) | 12(6) | -6(6) |
| C(6) | 126(7) | 107(8) | 165(7) | -15(6) | -9(6) | -23(6) |
| C(7) | 142(8) | 130(8) | 189(8) | -18(6) | -23(6) | -54(6) |
| C(8) | 150(8) | 160(9) | 154(7) | -27(6) | -29(6) | -25(6) |
| C(9) | 113(7) | 112(8) | 175(7) | -9(6) | -14(6) | -23(6) |
| C(10) | 114(7) | 118(8) | 159(7) | -5(6) | -16(6) | -3(6) |
| C(11) | 98(7) | 99(8) | 174(7) | 0(6) | -7(6) | 3(6) |
| C(12) | 119(7) | 125(8) | 159(7) | 20(6) | -10(6) | -2(6) |
| C(13) | 105(7) | 90(7) | 208(8) | 6(6) | -21(6) | -9(6) |
| C(14) | 104(7) | 85(7) | 193(8) | -8(6) | -14(6) | 5(6) |
| C(15) | 111(7) | 106(8) | 203(8) | -22(6) | -5(6) | 1(6) |
| C(16) | 123(7) | 106(8) | 197(8) | -20(6) | -15(6) | -11(6) |
| C(17) | 156(8) | 123(8) | 213(8) | -56(7) | -20(6) | -26(6) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(18) | 178(8) | 122(8) | 190(8) | -48(6) | -25(6) | -5(7) |
| C(19) | 155(8) | 123(8) | 170(7) | -25(6) | -18(6) | -8(6) |
| C(20) | 124(7) | 109(8) | 151(7) | -18(6) | -2(6) | -37(6) |
| C(21) | 138(8) | 140(8) | 169(7) | -41(6) | -7(6) | -22(6) |
| C(22) | 274(10) | 108(8) | 162(8) | -23(6) | -51(7) | -39(7) |
| C(23) | 272(10) | 208(10) | 144(8) | 0(7) | -35(7) | -148(8) |
| C(24) | 148(8) | 296(11) | 196(8) | -14(8) | -4(7) | -78(7) |
| C(25) | 143(8) | 160(9) | 193(8) | -9(7) | -12(6) | -13(7) |
| C(26) | 124(7) | 124(8) | 163(7) | -3(6) | -8(6) | -27(6) |
| C(27) | 123(7) | 146(8) | 191(8) | -7(6) | -29(6) | 2(6) |
| C(28) | 126(8) | 191(9) | 186(8) | -37(7) | 9(6) | -7(7) |
| C(29) | 168(8) | 205(9) | 147(7) | 4(6) | -11(6) | -30(7) |
| C(30) | 146(8) | 164(9) | 196(8) | 25(7) | -40(6) | 11(7) |
| C(31) | 127(8) | 136(8) | 178(7) | 5(6) | -2(6) | 6(6) |
| C(32) | 120(7) | 131(8) | 193(8) | -36(6) | -2(6) | -36(6) |
| C(33) | 124(8) | 187(9) | 189(8) | -39(7) | -7(6) | -14(7) |
| C(34) | 121(8) | 295(11) | 185(8) | -54(7) | -10(6) | -69(7) |
| C(35) | 216(9) | 200(10) | 248(9) | -66(8) | 8(7) | -125(7) |
| C(36) | 174(9) | 132(9) | 390(11) | -78(8) | 25(8) | -39(7) |
| C(37) | 101(7) | 137(9) | 342(10) | -61(7) | 11(7) | -30(6) |
| C(38) | 255(12) | 306(13) | 744(19) | -363(13) | -220(13) | 142(10) |
| C(39) | 141(9) | 173(10) | 442(12) | -25(9) | -81(8) | -12(7) |
| C(40) | 314(14) | 501(16) | 371(13) | 260(11) | 116(10) | 263(13) |
| C(41) | 484(16) | 506(16) | 183(9) | -82(10) | -62(10) | 369(14) |
| C(42) | 148(11) | 165(12) | 1890(40) | -226(19) | -310(19) | 36(9) |
| C(43) | 299(12) | 375(13) | 201(9) | 89(9) | 3(8) | 183(10) |
| C(51) | 294(13) | 344(13) | 441(14) | 38(11) | -160(11) | -26(10) |
| Cl(1) | 263(3) | 385(3) | 561(4) | 75(3) | -177(3) | -59(2) |
| Cl(2) | 357(4) | 439(4) | 939(6) | 212(4) | -351(4) | -142(3) |
| C(52) | 730(20) | 363(16) | 400(15) | 20(12) | 28(14) | -6(15) |
| Cl(3) | 510(4) | 625(5) | 329(3) | -29(3) | -55(3) | -61(4) |
| Cl(4) | 449(4) | 512(5) | 669(5) | -5(4) | 97(4) | -144(3) |
| C(53) | 680(20) | 389(17) | 439(16) | -86(13) | 63(15) | 61(15) |
| Cl(5A) | 495(9) | 594(10) | 576(9) | -269(7) | -42(7) | -169(7) |
| Cl(6A) | 584(10) | 370(8) | 548(8) | -87(6) | 185(7) | -46(6) |
| Cl(5B) | 313(7) | 568(9) | 330(6) | -77(6) | -73(5) | 78(6) |
| Cl(6B) | 396(8) | 577(10) | 763(11) | -344(9) | -234(8) | 84(7) |

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Date 24 January 2008

**Crystal Structure Analysis of:**
**1-Ir(py)$_2$**
(shown below)

**For** Investigator: Joshua Palmer ext. 6332
Advisor: H. B. Gray ext. 6500
Account Number: HGB.BP-1-BP.AMOCO
**By** Michael W. Day 116 Beckman ext. 2734
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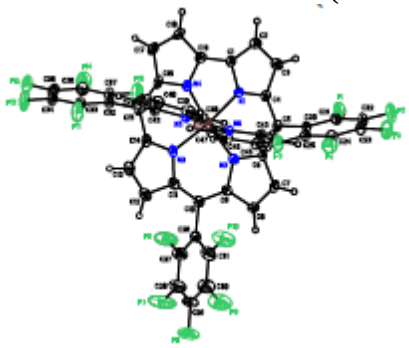

**1-Ir(py)$_2$**

**Note:** The crystallographic data have been deposited in the Cambridge Database (CCDC) and have been placed on hold pending further instructions from me. The deposition number is 657603. Ideally the CCDC would like the publication to contain a footnote of the type: "Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 657603".

Table C-3-1. Crystal data and structure refinement for **1-Ir(py)$_2$** (CCDC 657603)

| | |
|---|---|
| Empirical formula | $C_{47}H_{18}N_6F_{15}Ir$, $3(CH_4O)$ |
| Formula weight | 1240.00 |
| Crystallization Solvent | Methanol |
| Crystal Habit | Column |
| Crystal size | 0.31 x 0.12 x 0.07 mm$^3$ |
| Crystal color | Dark red |

**Data Collection**

| | |
|---|---|
| Type of diffractometer | Bruker KAPPA APEX II |
| Wavelength | 0.71073 Å MoKα |
| Data Collection Temperature | 100(2) K |
| θ range for 9608 reflections used in lattice determination | 2.39 to 32.74° |
| Unit cell dimensions | a = 48.016(2) Å<br>b = 8.7249(4) Å β= 124.247(2)°<br>c = 27.2703(13) Å |
| Volume | 9443.7(8) Å$^3$ |
| Z | 8 |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Density (calculated) | 1.744 Mg/m$^3$ |
| F(000) | 4864 |
| θ range for data collection | 1.81 to 32.95° |
| Completeness to θ = 32.95° | 98.5 % |
| Index ranges | $-73 \leq h \leq 72$, $-11 \leq k \leq 13$, $-40 \leq l \leq 41$ |
| Data collection scan type | ω scans; 21 settings |
| Reflections collected | 112588 |
| Independent reflections | 17484 [$R_{int}$= 0.0721] |
| Absorption coefficient | 2.938 mm$^{-1}$ |
| Absorption correction | None |
| Max. and min. transmission (calc) | 0.8208 and 0.4628 |

Table C-3-1 cont.

**Structure Solution and Refinement**

| | |
|---|---|
| Structure solution program | SHELXS-97 (Sheldrick, 1990) |
| Primary solution method | Patterson method |
| Secondary solution method | Difference Fourier map |
| Hydrogen placement | Geometric positions |
| Structure refinement program | SHELXL-97 (Sheldrick, 1997) |
| Refinement method | Full matrix least-squares on $F^2$ |
| Data / restraints / parameters | 17484 / 54 / 695 |
| Treatment of hydrogen atoms | Riding |
| Goodness-of-fit on $F^2$ | 1.520 |
| Final R indices [I>2σ(I), 12341 reflections] | R1 = 0.0441, *w*R2 = 0.0563 |
| R indices (all data) | R1 = 0.0761, *w*R2 = 0.0580 |
| Type of weighting scheme used | Sigma |
| Weighting scheme used | $w=1/\sigma^2(Fo^2)$ |
| Max shift/error | 0.007 |
| Average shift/error | 0.000 |
| Largest diff. peak and hole | 4.237 and -2.827 e.Å$^{-3}$ |

**Special Refinement Details**

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

The crystals contain methanol as a solvent of crystallization—three in the asymmetric unit. One of those three is disordered between two positions. The disorder was modeled with restraint on the C-O bond distances and on the anisotropic displacement parameters (ADP). In the solvent only C-O distances were restrained to have similar distances, the ADPs were restrained to mimic isotropic behavior, and for the disordered site the population was restrained so the occupancies summed to one.

Refinement of $F^2$ against ALL reflections. The weighted R-factor (*w*R) 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 $F^2 > 2\sigma(F^2)$ 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.

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.

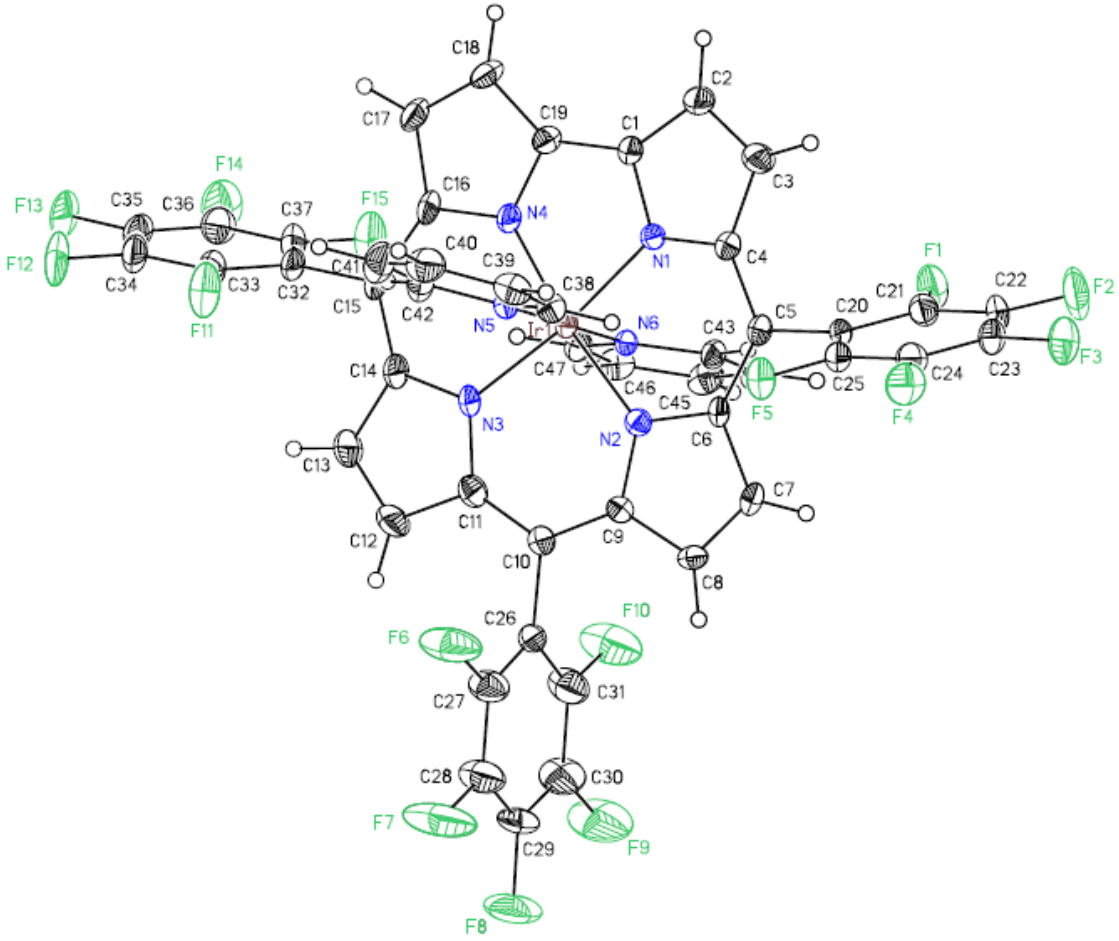

Table C-3-2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for **1-Ir(py)$_2$** (CCDC 657603). U(eq) is defined as the trace of the orthogonalized Uij tensor.

| | x | y | z | | $U_{eq}$ |
|---|---|---|---|---|---|
| Ir(1) | 5966(1) | 2657(1) | 37(1) | 17(1) | 1 |
| F(1) | 5516(1) | 3864(2) | 1516(1) | 36(1) | 1 |
| F(2) | 5321(1) | 2868(2) | 2209(1) | 50(1) | 1 |
| F(3) | 5304(1) | -171(2) | 2394(1) | 45(1) | 1 |
| F(4) | 5495(1) | -2227(2) | 1892(1) | 36(1) | 1 |
| F(5) | 5695(1) | -1256(2) | 1201(1) | 29(1) | 1 |
| F(6) | 7064(1) | -1186(2) | 1111(1) | 60(1) | 1 |
| F(7) | 7708(1) | -1870(2) | 1935(1) | 79(1) | 1 |
| F(8) | 8128(1) | 299(2) | 2706(1) | 67(1) | 1 |
| F(9) | 7893(1) | 3140(2) | 2662(1) | 79(1) | 1 |
| F(10) | 7246(1) | 3836(2) | 1831(1) | 66(1) | 1 |
| F(11) | 6131(1) | 1475(2) | -1786(1) | 44(1) | 1 |
| F(12) | 6229(1) | 2374(2) | -2618(1) | 48(1) | 1 |
| F(13) | 6261(1) | 5398(2) | -2813(1) | 44(1) | 1 |
| F(14) | 6212(1) | 7524(2) | -2139(1) | 50(1) | 1 |
| F(15) | 6118(1) | 6640(2) | -1299(1) | 44(1) | 1 |
| N(1) | 5548(1) | 2875(2) | -7(1) | 18(1) | 1 |
| N(2) | 6212(1) | 1834(2) | 853(1) | 17(1) | 1 |
| N(3) | 6356(1) | 2535(3) | -27(1) | 21(1) | 1 |
| N(4) | 5672(1) | 3499(2) | -758(1) | 19(1) | 1 |
| N(5) | 5804(1) | 504(2) | -333(1) | 19(1) | 1 |
| N(6) | 6125(1) | 4806(2) | 395(1) | 17(1) | 1 |
| C(1) | 5268(1) | 3338(3) | -542(1) | 20(1) | 1 |
| C(2) | 4995(1) | 3231(3) | -476(2) | 26(1) | 1 |
| C(3) | 5117(1) | 2679(3) | 84(1) | 27(1) | 1 |
| C(4) | 5474(1) | 2447(3) | 381(1) | 19(1) | 1 |
| C(5) | 5725(1) | 1839(3) | 948(1) | 19(1) | 1 |
| C(6) | 6070(1) | 1600(3) | 1170(1) | 16(1) | 1 |
| C(7) | 6342(1) | 1145(3) | 1757(1) | 19(1) | 1 |
| C(8) | 6631(1) | 1139(3) | 1778(1) | 19(1) | 1 |
| C(9) | 6552(1) | 1570(3) | 1205(1) | 16(1) | 1 |
| C(10) | 6765(1) | 1702(3) | 1000(1) | 21(1) | 1 |
| C(11) | 6678(1) | 2154(3) | 440(2) | 25(1) | 1 |
| C(12) | 6893(1) | 2367(4) | 223(2) | 38(1) | 1 |
| C(13) | 6694(1) | 2873(3) | -344(2) | 35(1) | 1 |
| C(14) | 6351(1) | 2996(3) | -511(2) | 26(1) | 1 |
| C(15) | 6066(1) | 3559(3) | -1046(1) | 24(1) | 1 |
| C(16) | 5735(1) | 3776(3) | -1179(1) | 21(1) | 1 |
| C(17) | 5416(1) | 4175(3) | -1707(1) | 25(1) | 1 |
| C(18) | 5178(1) | 4109(3) | -1579(1) | 24(1) | 1 |
| C(19) | 5340(1) | 3684(3) | -977(1) | 19(1) | 1 |
| C(20) | 5612(1) | 1341(3) | 1330(1) | 19(1) | 1 |
| C(21) | 5509(1) | 2351(3) | 1595(1) | 24(1) | 1 |
| C(22) | 5406(1) | 1847(3) | 1947(2) | 30(1) | 1 |
| C(23) | 5399(1) | 318(4) | 2045(2) | 30(1) | 1 |
| C(24) | 5497(1) | -717(3) | 1791(2) | 25(1) | 1 |
| C(25) | 5602(1) | -200(3) | 1442(1) | 23(1) | 1 |

| | | | | | |
|---|---|---|---|---|---|
| C(26) | 7129(1) | 1337(3) | 1446(1) | 21(1) | 1 |
| C(27) | 7262(1) | -81(3) | 1490(2) | 33(1) | 1 |
| C(28) | 7595(1) | -444(4) | 1909(2) | 42(1) | 1 |
| C(29) | 7804(1) | 637(4) | 2292(2) | 40(1) | 1 |
| C(30) | 7686(1) | 2067(4) | 2269(2) | 43(1) | 1 |
| C(31) | 7352(1) | 2408(4) | 1847(2) | 37(1) | 1 |
| C(32) | 6117(1) | 4024(3) | -1516(2) | 24(1) | 1 |
| C(33) | 6151(1) | 2980(3) | -1861(2) | 30(1) | 1 |
| C(34) | 6201(1) | 3435(4) | -2291(2) | 32(1) | 1 |
| C(35) | 6219(1) | 4956(4) | -2390(2) | 32(1) | 1 |
| C(36) | 6187(1) | 6030(4) | -2054(2) | 32(1) | 1 |
| C(37) | 6140(1) | 5553(3) | -1626(2) | 30(1) | 1 |
| C(38) | 5692(1) | -525(3) | -113(2) | 24(1) | 1 |
| C(39) | 5561(1) | -1926(3) | -378(2) | 29(1) | 1 |
| C(40) | 5536(1) | -2285(3) | -893(2) | 33(1) | 1 |
| C(41) | 5648(1) | -1245(3) | -1120(2) | 35(1) | 1 |
| C(42) | 5780(1) | 122(3) | -832(2) | 29(1) | 1 |
| C(43) | 6110(1) | 5276(3) | 851(1) | 20(1) | 1 |
| C(44) | 6235(1) | 6665(3) | 1127(1) | 26(1) | 1 |
| C(45) | 6378(1) | 7628(3) | 929(1) | 27(1) | 1 |
| C(46) | 6387(1) | 7189(3) | 451(2) | 26(1) | 1 |
| C(47) | 6258(1) | 5777(3) | 192(1) | 22(1) | 1 |
| | | | | | |
| C(51) | 7183(5) | 6190(20) | 349(12) | 179(11) | 0.314(3) |
| O(51) | 7428(5) | 5226(18) | 363(9) | 202(8) | 0.314(3) |
| | | | | | |
| C(52) | 7911(1) | 9259(6) | 1017(3) | 122(2) | 1 |
| O(52) | 7660(1) | 10415(4) | 759(2) | 123(2) | 1 |
| | | | | | |
| C(53) | 6840(2) | 8859(7) | 9592(4) | 84(2) | 0.686(3) |
| O(53) | 7116(1) | 9625(4) | 9631(2) | 83(2) | 0.686(3) |
| | | | | | |
| C(54) | 6988(2) | 865(6) | 8397(3) | 131(2) | 1 |
| O(54) | 7050(1) | 1778(4) | 8876(2) | 133(2) | 1 |

Table C-3-3. Selected bond lengths [Å] and angles [°] for **1-Ir(py)$_2$** (CCDC 657603)

| | | | |
|---|---|---|---|
| Ir(1)-N(4) | 1.947(2) | N(4)-Ir(1)-N(1) | 79.55(10) |
| Ir(1)-N(1) | 1.953(2) | N(4)-Ir(1)-N(2) | 172.23(10) |
| Ir(1)-N(2) | 1.976(2) | N(1)-Ir(1)-N(2) | 92.69(10) |
| Ir(1)-N(3) | 1.979(2) | N(4)-Ir(1)-N(3) | 92.92(10) |
| Ir(1)-N(6) | 2.052(2) | N(1)-Ir(1)-N(3) | 172.47(10) |
| Ir(1)-N(5) | 2.066(2) | N(2)-Ir(1)-N(3) | 94.84(10) |
| | | N(4)-Ir(1)-N(6) | 91.55(9) |
| | | N(1)-Ir(1)-N(6) | 91.87(9) |
| | | N(2)-Ir(1)-N(6) | 88.27(9) |
| | | N(3)-Ir(1)-N(6) | 88.60(9) |
| | | N(4)-Ir(1)-N(5) | 87.80(9) |
| | | N(1)-Ir(1)-N(5) | 88.04(9) |
| | | N(2)-Ir(1)-N(5) | 92.38(9) |
| | | N(3)-Ir(1)-N(5) | 91.41(9) |
| | | N(6)-Ir(1)-N(5) | 179.34(12) |

Table C-3-4. Bond lengths [Å] and angles [°] for **1-Ir(tma)$_2$** (CCDC 671270)

| | | | |
|---|---|---|---|
| Ir(1)-N(4) | 1.947(2) | C(15)-C(32) | 1.494(4) |
| Ir(1)-N(1) | 1.953(2) | C(16)-C(17) | 1.434(4) |
| Ir(1)-N(2) | 1.976(2) | C(17)-C(18) | 1.370(4) |
| Ir(1)-N(3) | 1.979(2) | C(18)-C(19) | 1.416(4) |
| Ir(1)-N(6) | 2.052(2) | C(20)-C(25) | 1.386(4) |
| Ir(1)-N(5) | 2.066(2) | C(20)-C(21) | 1.396(4) |
| F(1)-C(21) | 1.340(3) | C(21)-C(22) | 1.376(4) |
| F(2)-C(22) | 1.342(3) | C(22)-C(23) | 1.366(4) |
| F(3)-C(23) | 1.335(3) | C(23)-C(24) | 1.372(4) |
| F(4)-C(24) | 1.346(3) | C(24)-C(25) | 1.382(4) |
| F(5)-C(25) | 1.344(3) | C(26)-C(27) | 1.365(4) |
| F(6)-C(27) | 1.340(3) | C(26)-C(31) | 1.377(4) |
| F(7)-C(28) | 1.344(3) | C(27)-C(28) | 1.381(5) |
| F(8)-C(29) | 1.343(4) | C(28)-C(29) | 1.345(5) |
| F(9)-C(30) | 1.348(3) | C(29)-C(30) | 1.358(4) |
| F(10)-C(31) | 1.338(3) | C(30)-C(31) | 1.381(5) |
| F(11)-C(33) | 1.341(3) | C(32)-C(33) | 1.383(4) |
| F(12)-C(34) | 1.344(3) | C(32)-C(37) | 1.384(4) |
| F(13)-C(35) | 1.337(4) | C(33)-C(34) | 1.383(4) |
| F(14)-C(36) | 1.342(3) | C(34)-C(35) | 1.365(4) |
| F(15)-C(37) | 1.347(3) | C(35)-C(36) | 1.378(4) |
| N(1)-C(4) | 1.348(3) | C(36)-C(37) | 1.369(4) |
| N(1)-C(1) | 1.375(4) | C(38)-C(39) | 1.378(4) |
| N(2)-C(9) | 1.368(3) | C(39)-C(40) | 1.374(5) |
| N(2)-C(6) | 1.387(4) | C(40)-C(41) | 1.368(4) |
| N(3)-C(14) | 1.367(4) | C(41)-C(42) | 1.371(4) |
| N(3)-C(11) | 1.378(4) | C(43)-C(44) | 1.373(4) |
| N(4)-C(19) | 1.361(3) | C(44)-C(45) | 1.373(4) |
| N(4)-C(16) | 1.362(4) | C(45)-C(46) | 1.383(4) |
| N(5)-C(42) | 1.343(4) | C(46)-C(47) | 1.381(4) |
| N(5)-C(38) | 1.350(4) | C(51)-O(51) | 1.425(5) |
| N(6)-C(43) | 1.347(4) | C(52)-O(52) | 1.418(4) |
| N(6)-C(47) | 1.353(3) | C(53)-O(53) | 1.432(4) |
| C(1)-C(2) | 1.426(4) | C(54)-O(54) | 1.410(4) |
| C(1)-C(19) | 1.442(4) | | |
| C(2)-C(3) | 1.378(4) | N(4)-Ir(1)-N(1) | 79.55(10) |
| C(3)-C(4) | 1.437(4) | N(4)-Ir(1)-N(2) | 172.23(10) |
| C(4)-C(5) | 1.424(4) | N(1)-Ir(1)-N(2) | 92.69(10) |
| C(5)-C(6) | 1.422(4) | N(4)-Ir(1)-N(3) | 92.92(10) |
| C(5)-C(20) | 1.482(4) | N(1)-Ir(1)-N(3) | 172.47(10) |
| C(6)-C(7) | 1.440(4) | N(2)-Ir(1)-N(3) | 94.84(10) |
| C(7)-C(8) | 1.359(4) | N(4)-Ir(1)-N(6) | 91.55(9) |
| C(8)-C(9) | 1.433(4) | N(1)-Ir(1)-N(6) | 91.87(9) |
| C(9)-C(10) | 1.421(4) | N(2)-Ir(1)-N(6) | 88.27(9) |
| C(10)-C(11) | 1.395(4) | N(3)-Ir(1)-N(6) | 88.60(9) |
| C(10)-C(26) | 1.497(4) | N(4)-Ir(1)-N(5) | 87.80(9) |
| C(11)-C(12) | 1.462(4) | N(1)-Ir(1)-N(5) | 88.04(9) |
| C(12)-C(13) | 1.354(5) | N(2)-Ir(1)-N(5) | 92.38(9) |
| C(13)-C(14) | 1.445(4) | N(3)-Ir(1)-N(5) | 91.41(9) |
| C(14)-C(15) | 1.413(4) | N(6)-Ir(1)-N(5) | 179.34(12) |
| C(15)-C(16) | 1.427(4) | C(4)-N(1)-C(1) | 112.4(2) |

| | | | |
|---|---|---|---|
| C(4)-N(1)-Ir(1) | 130.07(19) | C(17)-C(18)-C(19) | 108.2(3) |
| C(1)-N(1)-Ir(1) | 116.8(2) | N(4)-C(19)-C(18) | 106.4(3) |
| C(9)-N(2)-C(6) | 110.5(2) | N(4)-C(19)-C(1) | 112.3(3) |
| C(9)-N(2)-Ir(1) | 124.9(2) | C(18)-C(19)-C(1) | 141.2(3) |
| C(6)-N(2)-Ir(1) | 124.27(19) | C(25)-C(20)-C(21) | 115.5(3) |
| C(14)-N(3)-C(11) | 111.4(2) | C(25)-C(20)-C(5) | 120.8(3) |
| C(14)-N(3)-Ir(1) | 124.5(2) | C(21)-C(20)-C(5) | 123.7(2) |
| C(11)-N(3)-Ir(1) | 123.62(19) | F(1)-C(21)-C(22) | 118.5(3) |
| C(19)-N(4)-C(16) | 111.8(3) | F(1)-C(21)-C(20) | 119.4(3) |
| C(19)-N(4)-Ir(1) | 118.0(2) | C(22)-C(21)-C(20) | 122.1(3) |
| C(16)-N(4)-Ir(1) | 129.7(2) | F(2)-C(22)-C(23) | 119.6(3) |
| C(42)-N(5)-C(38) | 117.3(3) | F(2)-C(22)-C(21) | 119.8(3) |
| C(42)-N(5)-Ir(1) | 120.9(2) | C(23)-C(22)-C(21) | 120.6(3) |
| C(38)-N(5)-Ir(1) | 121.6(2) | F(3)-C(23)-C(22) | 120.6(3) |
| C(43)-N(6)-C(47) | 117.9(2) | F(3)-C(23)-C(24) | 120.1(3) |
| C(43)-N(6)-Ir(1) | 121.29(19) | C(22)-C(23)-C(24) | 119.3(3) |
| C(47)-N(6)-Ir(1) | 120.8(2) | F(4)-C(24)-C(23) | 119.9(3) |
| N(1)-C(1)-C(2) | 105.5(3) | F(4)-C(24)-C(25) | 120.4(3) |
| N(1)-C(1)-C(19) | 113.0(3) | C(23)-C(24)-C(25) | 119.7(3) |
| C(2)-C(1)-C(19) | 141.4(3) | F(5)-C(25)-C(24) | 117.6(2) |
| C(3)-C(2)-C(1) | 108.2(3) | F(5)-C(25)-C(20) | 119.7(3) |
| C(2)-C(3)-C(4) | 107.8(3) | C(24)-C(25)-C(20) | 122.8(3) |
| N(1)-C(4)-C(5) | 121.2(3) | C(27)-C(26)-C(31) | 115.5(3) |
| N(1)-C(4)-C(3) | 106.0(3) | C(27)-C(26)-C(10) | 122.6(3) |
| C(5)-C(4)-C(3) | 132.7(3) | C(31)-C(26)-C(10) | 122.0(3) |
| C(6)-C(5)-C(4) | 126.1(3) | F(6)-C(27)-C(26) | 119.3(3) |
| C(6)-C(5)-C(20) | 117.1(3) | F(6)-C(27)-C(28) | 117.6(3) |
| C(4)-C(5)-C(20) | 116.7(3) | C(26)-C(27)-C(28) | 123.1(3) |
| N(2)-C(6)-C(5) | 125.4(3) | F(7)-C(28)-C(29) | 120.4(3) |
| N(2)-C(6)-C(7) | 106.0(2) | F(7)-C(28)-C(27) | 120.1(3) |
| C(5)-C(6)-C(7) | 128.6(3) | C(29)-C(28)-C(27) | 119.5(3) |
| C(8)-C(7)-C(6) | 108.4(3) | F(8)-C(29)-C(28) | 120.3(3) |
| C(7)-C(8)-C(9) | 108.3(3) | F(8)-C(29)-C(30) | 119.8(3) |
| N(2)-C(9)-C(10) | 123.3(3) | C(28)-C(29)-C(30) | 119.8(3) |
| N(2)-C(9)-C(8) | 106.8(2) | F(9)-C(30)-C(29) | 119.9(3) |
| C(10)-C(9)-C(8) | 129.9(3) | F(9)-C(30)-C(31) | 120.3(3) |
| C(11)-C(10)-C(9) | 127.9(3) | C(29)-C(30)-C(31) | 119.8(3) |
| C(11)-C(10)-C(26) | 116.4(3) | F(10)-C(31)-C(26) | 119.7(3) |
| C(9)-C(10)-C(26) | 115.7(3) | F(10)-C(31)-C(30) | 118.0(3) |
| N(3)-C(11)-C(10) | 124.8(3) | C(26)-C(31)-C(30) | 122.3(3) |
| N(3)-C(11)-C(12) | 105.9(3) | C(33)-C(32)-C(37) | 115.7(3) |
| C(10)-C(11)-C(12) | 129.3(3) | C(33)-C(32)-C(15) | 123.0(3) |
| C(13)-C(12)-C(11) | 107.5(3) | C(37)-C(32)-C(15) | 121.3(3) |
| C(12)-C(13)-C(14) | 109.1(3) | F(11)-C(33)-C(34) | 118.2(3) |
| N(3)-C(14)-C(15) | 125.3(3) | F(11)-C(33)-C(32) | 119.7(3) |
| N(3)-C(14)-C(13) | 106.0(3) | C(34)-C(33)-C(32) | 122.1(3) |
| C(15)-C(14)-C(13) | 128.6(3) | F(12)-C(34)-C(35) | 120.0(3) |
| C(14)-C(15)-C(16) | 127.1(3) | F(12)-C(34)-C(33) | 119.7(3) |
| C(14)-C(15)-C(32) | 116.5(3) | C(35)-C(34)-C(33) | 120.3(3) |
| C(16)-C(15)-C(32) | 116.4(3) | F(13)-C(35)-C(34) | 120.3(3) |
| N(4)-C(16)-C(15) | 120.3(3) | F(13)-C(35)-C(36) | 120.4(3) |
| N(4)-C(16)-C(17) | 105.7(3) | C(34)-C(35)-C(36) | 119.3(3) |
| C(15)-C(16)-C(17) | 133.9(3) | F(14)-C(36)-C(37) | 121.2(3) |
| C(18)-C(17)-C(16) | 107.9(3) | F(14)-C(36)-C(35) | 119.4(3) |

| | | | |
|---|---|---|---|
| C(37)-C(36)-C(35) | 119.4(3) | C(40)-C(41)-C(42) | 119.4(3) |
| F(15)-C(37)-C(36) | 117.5(3) | N(5)-C(42)-C(41) | 122.9(3) |
| F(15)-C(37)-C(32) | 119.3(3) | N(6)-C(43)-C(44) | 122.8(3) |
| C(36)-C(37)-C(32) | 123.3(3) | C(43)-C(44)-C(45) | 119.0(3) |
| N(5)-C(38)-C(39) | 122.2(3) | C(44)-C(45)-C(46) | 119.2(3) |
| C(40)-C(39)-C(38) | 119.4(3) | C(47)-C(46)-C(45) | 119.2(3) |
| C(41)-C(40)-C(39) | 118.7(3) | N(6)-C(47)-C(46) | 121.9(3) |

Table C-3-5. Anisotropic displacement parameters ($Å^2$ x $10^4$) for **1-Ir(py)$_2$** (CCDC 657603). The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [ $h^2 a^{*2} U^{11}$ + ... + 2 h k a* b* $U^{12}$ ].

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ir(1) | 170(1) | 230(1) | 136(1) | 13(1) | 103(1) | 8(1) |
| F(1) | 488(14) | 323(10) | 423(14) | 21(8) | 345(12) | 83(8) |
| F(2) | 695(16) | 565(12) | 531(15) | 27(10) | 528(14) | 154(10) |
| F(3) | 524(15) | 679(13) | 383(14) | 115(10) | 396(14) | 18(10) |
| F(4) | 411(12) | 362(10) | 380(12) | 95(9) | 266(11) | -37(9) |
| F(5) | 405(12) | 266(9) | 325(12) | -23(8) | 277(11) | -17(8) |
| F(6) | 274(13) | 413(12) | 699(19) | -202(11) | 25(13) | 32(9) |
| F(7) | 323(14) | 533(13) | 950(20) | -92(13) | 21(15) | 173(10) |
| F(8) | 167(13) | 908(16) | 600(20) | -107(13) | 19(13) | 68(11) |
| F(9) | 318(14) | 775(15) | 830(20) | -448(14) | 53(15) | -113(11) |
| F(10) | 357(14) | 452(12) | 840(20) | -272(12) | 138(15) | 1(10) |
| F(11) | 701(16) | 372(11) | 456(15) | -71(9) | 462(14) | -80(10) |
| F(12) | 677(15) | 607(12) | 393(13) | -136(11) | 444(13) | -73(11) |
| F(13) | 524(15) | 686(13) | 313(13) | 85(10) | 359(13) | -10(10) |
| F(14) | 695(15) | 452(11) | 523(15) | 125(11) | 451(14) | 32(11) |
| F(15) | 680(16) | 386(10) | 460(15) | -35(10) | 447(14) | -17(10) |
| N(1) | 145(13) | 257(13) | 150(13) | 20(10) | 94(12) | 1(9) |
| N(2) | 181(14) | 153(11) | 176(14) | -2(9) | 101(12) | 7(9) |
| N(3) | 217(13) | 287(13) | 190(13) | -5(11) | 158(12) | 7(11) |
| N(4) | 195(14) | 243(12) | 159(14) | 11(10) | 122(12) | -11(10) |
| N(5) | 177(14) | 258(13) | 160(14) | 16(10) | 106(13) | 44(10) |
| N(6) | 155(14) | 258(12) | 133(13) | 37(10) | 99(12) | 27(10) |
| C(1) | 192(17) | 252(15) | 160(16) | -3(12) | 109(15) | 3(12) |
| C(2) | 167(17) | 393(17) | 202(18) | -19(14) | 89(16) | -22(13) |
| C(3) | 190(16) | 356(17) | 261(17) | 34(15) | 134(15) | 1(14) |
| C(4) | 207(15) | 223(14) | 163(14) | 12(13) | 112(13) | 12(13) |
| C(5) | 230(17) | 200(14) | 167(16) | 11(11) | 136(15) | -12(11) |
| C(6) | 220(17) | 155(13) | 165(16) | -3(11) | 143(14) | 1(11) |
| C(7) | 283(19) | 176(14) | 150(16) | -16(11) | 139(16) | -8(12) |
| C(8) | 152(16) | 200(14) | 165(17) | 11(11) | 57(14) | 17(11) |
| C(9) | 160(16) | 145(13) | 185(16) | 1(11) | 101(14) | -12(11) |
| C(10) | 197(17) | 264(15) | 202(18) | 8(12) | 125(15) | 11(12) |
| C(11) | 210(17) | 314(16) | 266(18) | -1(13) | 166(16) | -16(13) |
| C(12) | 240(18) | 640(20) | 330(20) | 114(19) | 209(17) | 117(18) |
| C(13) | 320(20) | 550(20) | 300(20) | 86(16) | 257(19) | 50(16) |
| C(14) | 269(19) | 370(18) | 225(18) | 19(13) | 194(17) | -3(13) |
| C(15) | 300(20) | 293(16) | 179(17) | -13(13) | 174(17) | -16(13) |
| C(16) | 275(19) | 255(15) | 157(17) | -21(12) | 157(16) | -46(12) |
| C(17) | 280(20) | 327(17) | 139(17) | 4(13) | 115(16) | -29(13) |
| C(18) | 208(18) | 318(16) | 132(17) | 21(12) | 54(15) | -35(12) |
| C(19) | 186(17) | 208(14) | 168(17) | -1(11) | 87(15) | -15(11) |
| C(20) | 148(16) | 288(16) | 151(16) | 11(12) | 104(14) | 11(12) |
| C(21) | 260(17) | 262(16) | 246(16) | 27(14) | 164(15) | 39(13) |
| C(22) | 300(20) | 444(19) | 260(20) | -14(14) | 216(18) | 77(14) |
| C(23) | 290(20) | 500(20) | 240(20) | 76(15) | 215(18) | 24(15) |
| C(24) | 235(19) | 313(17) | 250(20) | 61(13) | 167(17) | -8(13) |
| C(25) | 204(18) | 321(17) | 191(18) | -29(13) | 123(16) | -1(13) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(26) | 162(17) | 307(16) | 191(18) | 12(13) | 111(15) | -13(12) |
| C(27) | 210(20) | 345(18) | 360(20) | -69(15) | 106(19) | -32(14) |
| C(28) | 270(20) | 390(20) | 460(30) | -37(17) | 120(20) | 73(16) |
| C(29) | 124(19) | 600(20) | 340(20) | -35(18) | 58(19) | 34(16) |
| C(30) | 219(19) | 480(20) | 440(30) | -191(17) | 96(19) | -136(16) |
| C(31) | 266(19) | 377(19) | 440(20) | -70(18) | 173(18) | -1(16) |
| C(32) | 236(19) | 384(18) | 169(18) | 6(13) | 148(16) | -6(13) |
| C(33) | 330(20) | 390(19) | 253(19) | -25(14) | 209(18) | -59(14) |
| C(34) | 320(20) | 490(20) | 230(20) | -60(16) | 205(18) | -34(15) |
| C(35) | 270(20) | 550(20) | 200(20) | 58(16) | 166(18) | -15(16) |
| C(36) | 320(20) | 393(19) | 300(20) | 83(15) | 208(19) | 12(15) |
| C(37) | 360(20) | 373(18) | 250(20) | -11(14) | 225(19) | 37(15) |
| C(38) | 231(19) | 258(16) | 233(19) | 5(13) | 140(16) | 22(12) |
| C(39) | 227(18) | 268(17) | 340(20) | 1(14) | 138(18) | 15(13) |
| C(40) | 299(19) | 279(17) | 320(20) | -65(16) | 115(17) | 12(15) |
| C(41) | 470(20) | 318(18) | 280(20) | -36(15) | 220(20) | 33(15) |
| C(42) | 390(20) | 294(17) | 240(20) | 6(14) | 213(19) | 51(14) |
| C(43) | 243(18) | 232(15) | 162(17) | 45(12) | 129(16) | 58(12) |
| C(44) | 330(20) | 254(15) | 170(17) | -19(13) | 131(16) | 32(13) |
| C(45) | 298(17) | 195(15) | 237(17) | -36(14) | 103(15) | -8(14) |
| C(46) | 238(17) | 230(16) | 275(18) | 31(13) | 121(16) | -21(13) |
| C(47) | 231(18) | 266(16) | 182(17) | 36(12) | 129(16) | 16(12) |
| | | | | | | |
| C(51) | 1790(120) | 1790(120) | 1800(120) | -110(40) | 1020(70) | 30(40) |
| O(51) | 2030(90) | 1980(90) | 2020(90) | 0(40) | 1130(60) | -20(40) |
| | | | | | | |
| C(52) | 990(30) | 1390(30) | 1380(40) | -20(30) | 730(30) | 260(30) |
| O(52) | 1170(30) | 1270(20) | 1180(30) | 50(20) | 630(20) | 240(20) |
| | | | | | | |
| C(53) | 990(40) | 840(30) | 820(40) | -120(30) | 580(30) | -190(30) |
| O(53) | 950(30) | 880(30) | 720(30) | -40(20) | 500(30) | 130(20) |
| | | | | | | |
| C(54) | 1430(40) | 1350(40) | 1220(40) | -90(30) | 800(30) | -10(30) |
| O(54) | 1610(30) | 1240(20) | 1190(30) | -120(20) | 810(30) | 180(20) |

Table C-3-6. Hydrogen bonds for **1-Ir(py)$_2$** (CCDC 657603) [Å and °]

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(51)-H(51)...O(54)#1 | 0.84 | 2.25 | 2.791(19) | 122.4 |
| O(52)-H(52)...O(54)#2 | 0.84 | 1.89 | 2.714(6) | 168.1 |
| O(53)-H(53)...O(52)#3 | 0.84 | 2.04 | 2.777(7) | 146.7 |
| O(54)-H(54)...O(51)#1 | 0.84 | 2.25 | 2.791(19) | 122.7 |

Symmetry transformations used to generate equivalent atoms:
#1 -x+3/2,-y+1/2,-z+1
#2 -x+3/2,-y+3/2,-z+1
#3 x,y,z+1