# Chapter 6. Appendices

## 6.1 Data collection and processing parameters

| complexes | **1.68** | **1.72** | **1.72$_{Et}$** | **2.1** |
|---|---|---|---|---|
| formula | $C_{16}H_{27}F_6PRuS_3$ | $C_{30}H_{54}I_2ORu_2S_6$ | $C_{36}H_{62}F_{12}N_2P_2Ru_2S_6$ | $C_{18}H_{29}Cl_3N_2Ru_2S_3$ |
| $M_r$ | 561.60 | 1079.03 | 1207.32 | 678.10 |
| temp, K | 295(2) | 223(2) | 223(2) | 295(2) |
| cryst color and habit | red, orthorhombic | red, cuboid | red, cuboid | black, orthorhombic |
| cryst size, mm | 0.36 × 0.14 × 0.06 | 0.36 × 0.10 × 0.10 | 0.16 × 0.10 × 0.10 | 0.39 × 0.28 × 0.25 |
| cryst system | Monoclinic | Monoclinic | Triclinic | Orthorhombic |
| space group | Cc | $P2_1/n$ | $P\bar{1}$ | Pnma |
| $a$, Å | 12.4124(9) | 12.3223(8) | 9.7797(12) | 18.6064(7) |
| $b$, Å | 13.5054(9) | 12.7391(9) | 12.2045(15) | 11.6704(5) |
| $c$, Å | 13.3056(9) | 14.4202(10) | 12.4609(15) | 11.2726(5) |
| $\alpha$, deg | 90 | 90 | 69.816(2) | 90 |
| $\beta$, deg | 105.499(2) | 112.007(2) | 69.704(2) | 90 |
| $\gamma$, deg | 90 | 90 | 66.951(2) | 90 |
| $V$, Å$^3$ | 2149.4(3) | 2098.7(2) | 1245.3(3) | 2447.78(18) |
| $Z$ | 4 | 2 | 1 | 4 |
| density, g cm$^{-3}$ | 1.735 | 1.708 | 1.610 | 1.840 |
| abs. coeff, mm$^{-1}$ | 1.146 | 2.510 | 0.996 | 1.826 |
| $F$(000) | 1136 | 1064 | 614 | 1352 |
| $\theta$ range for data collection | 2.27 to 25.00 | 1.86 to 25.00 | 1.80 to 25.00 | 2.11 to 27.50 |
| index ranges | –10<=h<=14, –16<=k<=15, –15<=l<=15 | –14<=h<=14, –15<=k<=14, –17<=l<=13 | –11<=h<=11, –14<=k<=14, –14<=l<=14 | –24<=h<=24, –15<=k<=9, –14<=l<=14 |
| no. of reflns collected | 6037 | 12020 | 10147 | 16704 |
| indep reflns | 2604 | 3685 | 4384 | 2949 |
| max. and min. transmission | 0.9344 and 0.6832 | 0.8307 and 0.4903 | 0.9350 and 0.6141 | 0.6582 and 0.5361 |
| no. of data/restraints/params | 2604 / 215 / 248 | 3685 / 62 / 182 | 4384 / 93 / 286 | 2949 / 0 / 162 |
| final $R$ indices [$I>2\sigma(I)$] [a, b] | R1 = 0.0385, wR2 = 0.0973 | R1 = 0.0553, wR2 = 0.1485 | R1 = 0.0622, wR2 = 0.1366 | R1 = 0.0247, wR2 = 0.0619 |
| $R$ indices (all data) | R1 = 0.0400, wR2 = 0.0985 | R1 = 0.0706, wR2 = 0.1561 | R1 = 0.0780, wR2 = 0.1429 | R1 = 0.0268, wR2 = 0.0630 |
| goodness-of-fit on F$^2$ [c] | 1.049 | 1.086 | 1.023 | 1.111 |
| large diff peak and hole, e Å$^{-3}$ | 0.681 and –0.416 | 1.868 and –0.591 | 1.165 and –0.685 | 0.394 and –0.582 |

[a] $R = (\Sigma||F_o| - |F_c||)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. [c] $\mathrm{GoF} = [(\Sigma\omega|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$

| complexes | **2.2** | **2.4** | **2.5** | **2.6A** |
|---|---|---|---|---|
| formula | $C_{37}H_{58}Cl_4Ru_3S_3$ | $C_{30}H_{49}ClF_{12}P_2Ru_3S_6$ | $C_{38}H_{64}F_{12}NiO_2P_2Ru_2S_6$ | $C_{38}H_{64}F_{12}N_3P_2PdRu_2S_6$ |
| $M_r$ | 1044.02 | 1230.65 | 648.02 | 1353.76 |
| temp, K | 223(2) | 223(2) | 294(2) | 223(2) |
| cryst color and habit | red, needle | black, orthorhombic | black, orthorhombic | red, orthorhombic |
| cryst size, mm | 0.40 × 0.08 × 0.06 | 0.20 × 0.09 × 0.04 | 0.22 × 0.16 × 0.14 | 0.36 × 0.20 × 0.12 |
| cryst system | Orthorhombic | Triclinic | Triclinic | Triclinic |
| space group | Pnnm | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$, Å | 14.4849(11) | 10.4075(5) | 10.1593(18) | 12.6299(6) |
| $b$, Å | 16.5260(12) | 13.2588(7) | 10.5154(19) | 13.5296(7) |
| $c$, Å | 17.2483(13) | 16.5211(8) | 12.654(2) | 15.4990(8) |
| $\alpha$, deg | 90 | 71.336(1) | 81.386(4) | 75.975(1) |
| $\beta$, deg | 90 | 83.199(1) | 70.138(4) | 80.759(1) |
| $\gamma$, deg | 90 | 76.937(1) | 76.824(4) | 89.513(1) |
| $V$, Å$^3$ | 4128.9(5) | 2101.36(18) | 1234.1(4) | 2534.9(2) |
| $Z$ | 4 | 2 | 2 | 2 |
| density, g cm$^{-3}$ | 1.680 | 1.945 | 1.744 | 1.774 |
| abs. coeff, mm$^{-1}$ | 1.520 | 1.580 | 1.379 | 1.326 |
| $F$(000) | 2112 | 1224 | 658 | 1362 |
| $\theta$ range for data collection | 1.71 to 25.00 | 1.65 to 25.00 | 1.72 to 27.57 | 1.55 to 25.00 |
| index ranges | –17<=h<=16, –19<=k<=19, –17<=l<=20 | –12<=h<=12, –15<=k<=15, –19<=l<=19 | –13<=h<=13, –13<=k<=12, –16<=l<=13 | –15<=h<=15, –16<=k<=16, –18<=l<=18 |
| no. of reflns collected | 22596 | 22757 | 8164 | 27446 |
| indep reflns | 3780 | 7402 | 5630 | 8909 |
| max. and min. transmission | 0.9143 and 0.5815 | 0.9213 and 0.7981 | 0.8303 and 0.7512 | 0.8571 and 0.6468 |
| no. of data/restraints/params | 3780 / 2 / 234 | 7402 / 213 / 553 | 5630 / 51 / 287 | 5402 / 0 / 219 |
| final $R$ indices [$I>2\sigma(I)$] [a, b] | R1 = 0.0745, wR2 = 0.1581 | R1 = 0.0452, wR2 = 0.0936 | R1 = 0.0690, wR2 = 0.1825 | R1 = 0.0328, wR2 = 0.0861 |
| $R$ indices (all data) | R1 = 0.0835, wR2 = 0.1617 | R1 = 0.0614, wR2 = 0.1001 | R1 = 0.1046, wR2 = 0.2003 | R1 = 0.0384, wR2 = 0.0884 |
| goodness-of-fit on F$^2$ [c] | 1.291 | 0.952 | 1.062 | 1.046 |
| large diff peak and hole, e Å$^{-3}$ | 1.247 and –1.680 | 3.285 and –0.686 | 0.909 and –0.663 | 1.083 and –0.846 |

[a] $R = (\Sigma||F_o| - |F_c||)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega||F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. [c] $\mathrm{GoF} = [(\Sigma\omega||F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$

| complexes | **2.7B** | **2.8** | **2.10** |
|---|---|---|---|
| formula | $C_{38}H_{61}F_{12}N_3P_2PtRu_2S_6$ | $C_{57}H_{63.50}F_{12}N_{2.50}P_4PtRuS_3$ | $C_{29}H_{43.50}F_{12}N_{0.50}P_2PdRu_2S_6$ |
| $M_r$ | 1439.43 | 1527.82 | 1189.98 |
| temp, K | 223(2) | 223(2) | 223(2) |
| cryst color and habit | yellow, cuboid | yellow, needle | red, orthorhombic |
| cryst size, mm | 0.34 × 0.12 × 0.10 | 0.50 × 0.40 × 0.24 | 0.38 × 0.20 × 0.10 |
| cryst system | Monoclinic | Triclinic | Triclinic |
| space group | P2/c | P $\bar{1}$ | P $\bar{1}$ |
| *a*, Å | 9.3529(10) | 12.4542(5) | 12.2103(4) |
| *b*, Å | 12.4153(13) | 13.7573(5) | 17.5255(6) |
| *c*, Å | 22.416(2) | 18.2964(7) | 22.4514(8) |
| $\alpha$, deg | 90 | 81.181(1) | 71.561(1) |
| $\beta$, deg | 93.236(2) | 85.885(1) | 75.592(1) |
| $\gamma$, deg | 90 | 88.486(1) | 72.138(1) |
| *V*, Å$^3$ | 2598.7(5) | 3089.4(2) | 4276.3(3) |
| *Z* | 2 | 2 | 4 |
| density, g cm$^{-3}$ | 1.840 | 1.642 | 1.848 |
| abs. coeff, mm$^{-1}$ | 3.636 | 2.786 | 1.557 |
| *F*(000) | 1420 | 1522 | 2356 |
| $\theta$ range for data collection | 1.64 to 25.00 | 1.73 to 25.00 | 1.26 to 25.00 |
| index ranges | –10<=h<=11, –10<=k<=14, –26<=l<=26 | –14<=h<=14, –16<=k<=16, –21<=l<=21 | –14<=h<=14, –20<=k<=20, –26<=l<=26 |
| no. of reflns collected | 14276 | 33361 | 46594 |
| indep reflns | 4505 | 10878 | 15068 |
| max. and min. transmission | 0.7125 and 0.3711 | 0.8652 and 0.7729 | 0.8599 and 0.5892 |
| no. of data/restraints/params | 4505 / 0 / 293 | 10878 / 135 / 684 | 15068 / 259 / 1011 |
| final *R* indices [$I>2\sigma(I)$] [a, b] | R1 = 0.0699, wR2 = 0.1760 | R1 = 0.0480, wR2 = 0.1300 | R1 = 0.0697, wR2 = 0.1599 |
| *R* indices (all data) | R1 = 0.0747, wR2 = 0.1783 | R1 = 0.0597, wR2 = 0.1345 | R1 = 0.1156, wR2 = 0.1810 |
| goodness-of-fit on F$^2$ [c] | 1.201 | 1.072 | 1.027 |
| large diff peak and hole, e Å$^{-3}$ | 3.825 and –1.289 | 1.917 and –1.133 | 1.366 and –1.223 |

[a] $R = (\Sigma||F_o| - |F_c||)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega||F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. [c] $\mathrm{GoF} = [(\Sigma\omega||F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$

| complexes | **2.11** | **2.12** | **2.13** |
|---|---|---|---|
| formula | $C_{35}H_{56.50}F_{12}N_{3.50}O_{0.50}P_2PtRu_2S_6$ | $C_{50}H_{53}F_{12}P_4PtRuS_3$ | $C_{34.50}H_{57}Cu_2F_{12}NO_{0.50}P_2Ru_2S_6$ |
| $M_r$ | 1413.87 | 1398.14 | 1305.33 |
| temp, K | 223(2) | 295(2) | 223(2) |
| cryst color and habit | dark blue, rectangular plate | black, needle | orange, cuboid |
| cryst size, mm | 0.20 × 0.10 × 0.04 | 0.44 × 0.14 × 0.10 | 0.40 × 0.20 × 0.10 |
| cryst system | Monoclinic | Monoclinic | Triclinic |
| space group | $P2_1/c$ | $P2_1/n$ | $P\bar{1}$ |
| *a*, Å | 10.2783(12) | 20.1037(19) | 12.8818(13) |
| *b*, Å | 25.882(3) | 11.4743(11) | 13.2769(14) |
| *c*, Å | 10.1807(12) | 25.903(3) | 16.2719(16) |
| $\alpha$, deg | 90 | 90 | 97.257(2) |
| $\beta$, deg | 112.954(2) | 92.489(2) | 100.978(2) |
| $\gamma$, deg | 90 | 90 | 111.208(2) |
| *V*, Å$^3$ | 2493.8(5) | 5969.6(10) | 2488.4(4) |
| *Z* | 2 | 4 | 2 |
| density, g cm$^{-3}$ | 1.883 | 1.556 | 1.742 |
| abs. coeff, mm$^{-1}$ | 3.788 | 2.875 | 1.828 |
| *F*(000) | 1390 | 2764 | 1310 |
| $\theta$ range for data collection | 2.15 to 24.00 | 1.57 to 25.00 | 1.68 to 27.50 |
| index ranges | –11<=h<=10, –29<=k<=24, –9<=l<=11 | –23<=h<=22, –13<=k<=13, –25<=l<=30 | –16<=h<=16, –17<=k<=17, –21<=l<=21 |
| no. of reflns collected | 12818 | 33754 | 32854 |
| indep reflns | 3873 | 10489 | 11424 |
| max. and min. transmission | 0.8632 and 0.5179 | 0.7620 and 0.3644 | 0.8384 and 0.5285 |
| no. of data/restraints/params | 3873 / 32 / 274 | 10489 / 1404 / 623 | 11424 / 21 / 587 |
| final *R* indices [$I>2\sigma(I)$] [a, b] | R1 = 0.0767, wR2 = 0.1624 | R1 = 0.0659, wR2 = 0.1700 | R1 = 0.0466, wR2 = 0.1211 |
| *R* indices (all data) | R1 = 0.0908, wR2 = 0.1672 | R1 = 0.1136, wR2 = 0.1939 | R1 = 0.0586, wR2 = 0.1271 |
| goodness-of-fit on F$^2$ [c] | 1.234 | 0.971 | 1.080 |
| large diff peak and hole, e Å$^{-3}$ | 1.801 and –4.748 | 1.509 and –1.441 | 1.090 and –0.535 |

[a] $R = (\Sigma||F_o| - |F_c||)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega||F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. [c] $\mathrm{GoF} = [(\Sigma\omega||F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$

| complexes | **2.13A** | **2.14** | **2.15** |
|---|---|---|---|
| formula | $C_{32}H_{52}Cu_2F_{12}O_{0.67}P_2Ru_2S_6$ | $C_{35}H_{59}Ag_2F_{12}NOP_2Ru_2S_6$ | $C_{34.50}H_{41.75}AuF_6N_{0.25}P_2RuS_3$ |
| $M_r$ | 1258.92 | 1410.01 | 1030.09 |
| temp, K | 223(2) | 223(2) | 223(2) |
| cryst color and habit | orange, cuboid | orange, cuboid | red, needle |
| cryst size, mm | 0.16 × 0.14 × 0.14 | 0.28 × 0.16 × 0.14 | 0.24 × 0.09 × 0.06 |
| cryst system | Tetragonal | Monoclinic | Triclinic |
| space group | P4/ncc | Cc | P $\bar{1}$ |
| *a*, Å | 23.7164(9) | 21.4107(16) | 8.9270(5) |
| *b*, Å | 23.7164(9) | 13.9823(11) | 14.3503(7) |
| *c*, Å | 49.973(4) | 17.6141(14) | 15.0100(8) |
| $\alpha$, deg | 90 | 90 | 88.792(1) |
| $\beta$, deg | 90 | 108.202(2) | 82.193(1) |
| $\gamma$, deg | 90 | 90 | 86.655(1) |
| *V*, Å$^3$ | 28108(3) | 5009.3(7) | 1901.6(2) |
| *Z* | 24 | 4 | 2 |
| density, g cm$^{-3}$ | 1.785 | 1.870 | 1.799 |
| abs. coeff, mm$^{-1}$ | 1.938 | 1.750 | 4.553 |
| *F*(000) | 15104 | 2800 | 1011 |
| $\theta$ range for data collection | 0.81 to 25.00 | 1.77 to 28.68 | 1.96 to 30.02 |
| index ranges | –28<=h<=28, –28<=k<=28, –48<=l<=59 | –24<=h<=28, –18<=k<=18, –23<=l<=13 | –12<=h<=12, –20<=k<=20, –21<=l<=21 |
| no. of reflns collected | 149596 | 15747 | 28972 |
| indep reflns | 12384 | 7812 | 11024 |
| max. and min. transmission | 0.7731 and 0.7468 | 0.8237 and 0.6805 | 0.7655 and 0.5998 |
| no. of data/restraints/params | 12384 / 95 / 828 | 7812 / 215 / 501 | 11024 / 432 / 496 |
| final *R* indices [$I>2\sigma(I)$] [a, b] | R1 = 0.0864, wR2 = 0.2372 | R1 = 0.0395, wR2 = 0.0790 | R1 = 0.0407, wR2 = 0.0551 |
| *R* indices (all data) | R1 = 0.1548, wR2 = 0.2798 | R1 = 0.0523, wR2 = 0.0807 | R1 = 0.0592, wR2 = 0.0576 |
| goodness-of-fit on F$^2$ [c] | 1.009 | 1.002 | 0.993 |
| large diff peak and hole, e Å$^{-3}$ | 2.838 and –0.920 | 0.915 and –0.455 | 1.620 and –1.563 |

[a] $R = (\Sigma||F_o| - |F_c||)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega||F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. [c] GoF $= [(\Sigma\omega||F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$

| complexes | **2.16** | **2.17** | **2.18** |
|---|---|---|---|
| formula | $C_{34}H_{56}Au_2F_{12}O_{0.50}P_2Ru_2S_6$ | $C_{28}H_{48}CuF_6OPRu_2S_6$ | $C_{28.25}H_{48}AgF_{12}O_{0.50}P_2Ru_2S_6$ |
| $M_r$ | 1551.16 | 1003.67 | 1187.98 |
| temp, K | 298(2) | 295(2) | 223(2) |
| cryst color and habit | orange, cuboid | black, needle | black, needle |
| cryst size, mm | 0.22 × 0.16 × 0.14 | 0.50 × 0.14 × 0.01 | 0.34 × 0.20 × 0.06 |
| cryst system | Monoclinic | Triclinic | Triclinic |
| space group | $P2_1/c$ | $P\bar{1}$ | $P\bar{1}$ |
| *a*, Å | 12.8833(9) | 8.935(2) | 12.2374(5) |
| *b*, Å | 23.5699(17) | 14.707(4) | 17.5939(7) |
| *c*, Å | 16.5363(12) | 17.053(4) | 22.0809(9) |
| $\alpha$, deg | 90 | 66.723(4) | 71.783(1) |
| $\beta$, deg | 99.254(2) | 76.713(5) | 74.961(1) |
| $\gamma$, deg | 90 | 81.282(5) | 72.241(1) |
| *V*, Å$^3$ | 4956.0(6) | 1998.7(9) | 4229.3(3) |
| *Z* | 4 | 2 | 4 |
| density, g cm$^{-3}$ | 2.079 | 1.668 | 1.866 |
| abs. coeff, mm$^{-1}$ | 6.889 | 1.677 | 1.612 |
| *F*(000) | 2976 | 1012 | 2362 |
| $\theta$ range for data collection | 1.73 to 25.00 | 2.35 to 25.00 | 1.91 to 27.50 |
| index ranges | –15<=h<=10, –26<=k<=28, –19<=l<=19 | –10<=h<=10, –17<=k<=17, –20<=l<=20 | –15<=h<=15, –21<=k<=22, –28<=l<=28 |
| no. of reflns collected | 28287 | 20997 | 29994 |
| indep reflns | 8722 | 7052 | 19260 |
| max. and min. transmission | 0.4824 and 0.3500 | 0.9834 and 0.4878 | 0.9095 and 0.6103 |
| no. of data/restraints/params | 8722 / 6 / 532 | 7052 / 50 / 473 | 19260 / 202 / 1075 |
| final *R* indices [$I>2\sigma(I)$] [a, b] | R1 = 0.0882, wR2 = 0.1845 | R1 = 0.0726, wR2 = 0.1631 | R1 = 0.0754, wR2 = 0.1486 |
| *R* indices (all data) | R1 = 0.0972, wR2 = 0.1883 | R1 = 0.1010, wR2 = 0.1744 | R1 = 0.1187, wR2 = 0.1650 |
| goodness-of-fit on F$^2$ [c] | 1.266 | 1.112 | 1.066 |
| large diff peak and hole, e Å$^{-3}$ | 2.691 and –1.783 | 0.823 and –0.968 | 1.243 and –0.798 |

[a] $R = (\Sigma||F_o| - |F_c||)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega||F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. [c] $\mathrm{GoF} = [(\Sigma\omega||F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$

| complexes | **2.19** | **2.20** | **2.22** | **2.23** |
|---|---|---|---|---|
| formula | $C_{32}H_{38}AuF_6P_2RuS_3$ | $C_{40}H_{54}AuF_6O_2P_2RuS_3$ | $C_{30}H_{39}ClF_6GeNPRuS_3$ | $C_{31}H_{42}F_6OPRuS_3Sn$ |
| $M_r$ | 992.78 | 1136.99 | 863.88 | 927.01 |
| temp, K | 295(2) | 223(2) | 223(2) | 294(2) |
| cryst color and habit | dark blue, needle | orange, cuboid | yellow, needle | yellow, cuboid |
| cryst size, mm | 0.34 × 0.12 × 0.10 | 0.20 × 0.10 × 0.08 | 0.14 × 0.08 × 0.04 | 0.22 × 0.18 × 0.12 |
| cryst system | Monoclinic | Triclinic | Orthorhombic | Monoclinic |
| space group | $P2_1/n$ | $P\bar{1}$ | Pbca | $P2_1/n$ |
| $a$, Å | 8.653(5) | 11.3788(7) | 16.0375(8) | 9.4442(14) |
| $b$, Å | 26.368(17) | 13.5233(8) | 14.6001(7) | 28.788(4) |
| $c$, Å | 15.926(9) | 15.4576(9) | 29.3549(15) | 13.275(2) |
| $\alpha$, deg | 90 | 76.609(1) | 90 | 90 |
| $\beta$, deg | 91.236(18) | 89.612(1) | 90 | 93.113(3) |
| $\gamma$, deg | 90 | 79.802(1) | 90 | 90 |
| $V$, Å$^3$ | 3633(4) | 2275.9(2) | 6873.4(6) | 3604.0(9) |
| $Z$ | 4 | 2 | 8 | 4 |
| density, g cm$^{-3}$ | 1.815 | 1.659 | 1.670 | 1.708 |
| abs. coeff, mm$^{-1}$ | 4.763 | 3.816 | 1.676 | 1.460 |
| $F$(000) | 1940 | 1130 | 3488 | 1856 |
| $\theta$ range for data collection | 1.49 to 25.00 | 1.82 to 25.00 | 1.39 to 25.00 | 1.69 to 27.58 |
| index ranges | –10<=h<=9, –31<=k<=31, –15<=l<=18 | –13<=h<=11, –15<=k<=16, –18<=l<=16 | –19<=h<=15, –17<=k<=17, –34<=l<=34 | –12<=h<=12, –37<=k<=35, –17<=l<=10 |
| no. of reflns collected | 20158 | 13092 | 38311 | 24216 |
| indep reflns | 6373 | 7967 | 6050 | 8287 |
| max. and min. transmission | 0.6474 and 0.2943 | 0.7500 and 0.5158 | 0.9277 and 0.8299 | 0.8442 and 0.7394 |
| no. of data/restraints/params | 6373 / 217 / 436 | 7967 / 70 / 501 | 6050 / 81 / 402 | 8282 / 80 / 434 |
| final $R$ indices [$I>2\sigma(I)$] [a, b] | R1 = 0.0984, wR2 = 0.2694 | R1 = 0.0856, wR2 = 0.1756 | R1 = 0.0493, wR2 = 0.0924 | R1 = 0.0541, wR2 = 0.1408 |
| $R$ indices (all data) | R1 = 0.1157, wR2 = 0.2817 | R1 = 0.0930, wR2 = 0.1789 | R1 = 0.0726, wR2 = 0.0969 | R1 = 0.0897, wR2 = 0.1558 |
| goodness-of-fit on F$^2$ [c] | 1.062 | 1.328 | 1.064 | 1.044 |
| large diff peak and hole, e Å$^{-3}$ | 7.082 and –3.147 | 2.101 and –3.632 | 0.940 and –0.778 | 1.972 and –0.613 |

[a] $R = (\Sigma||F_o| - |F_c||)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega||F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. [c] $\mathrm{GoF} = [(\Sigma\omega||F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$

| complexes | **2.24** | **2.25** | **2.27** | **2.28** |
|---|---|---|---|---|
| formula | $C_{34}H_{41}F_6PRuS_3Sn$ | $C_{34}H_{41}F_6PPbRuS_3$ | $C_{16}H_{29}F_6PRuS_3$ | $C_{19}H_{29}IN_2RuS_3$ |
| $M_r$ | 910.58 | 999.08 | 563.61 | 609.59 |
| temp, K | 293(2) | 223(2) | 223(2) | 223(2) |
| cryst color and habit | yellow, cuboid | orange, rhombus | yellow, cuboid | yellow, orthorhombic |
| cryst size, mm | 0.34 × 0.30 × 0.24 | 0.16 × 0.06 × 0.06 | 0.36 × 0.36 × 0.16 | 0.36 × 0.18 × 0.14 |
| cryst system | Orthorhombic | Orthorhombic | Monoclinic | Orthorhombic |
| space group | Pbca | Pbca | $P2_1/c$ | *P*nma |
| *a*, Å | 15.169(3) | 15.1660(7) | 12.4228(2) | 28.5808(8) |
| *b*, Å | 19.513(2) | 19.4435(8) | 9.0810(2) | 8.5395(2) |
| *c*, Å | 24.576(2) | 24.5810(10) | 19.9557(4) | 9.5463(3) |
| $\alpha$, deg | 90 | 90 | 90 | 90 |
| $\beta$, deg | 90 | 90 | 100.6460(10) | 90 |
| $\gamma$, deg | 90 | 90 | 90 | 90 |
| *V*, Å$^3$ | 7274.1(16) | 7248.4(5) | 2212.48(7) | 2329.92(11) |
| *Z* | 8 | 8 | 4 | 4 |
| density, g cm$^{-3}$ | 1.663 | 1.831 | 1.692 | 1.738 |
| abs. coeff, mm$^{-1}$ | 1.373 | 5.328 | 1.113 | 2.273 |
| *F*(000) | 3648 | 3904 | 1144 | 1208 |
| $\theta$ range for data collection | 1.66 to 30.03 | 1.66 to 30.51 | 2.08 to 30.01 | 2.25 to 28.28 |
| index ranges | –20<=h<=18, –18<=k<=27, –34<=l<=34 | –16<=h<=21, –27<=k<=27, –33<=l<=29 | –17<=h<=17, 0<=k<=12, 0<=l<=28 | 0<=h<=37, 0<=k<=11, 0<=l<=12 |
| no. of reflns collected | 56665 | 57376 | 20439 | 19389 |
| indep reflns | 10390 | 10647 | 6322 | 3080 |
| max. and min. transmission | 0.76230 and 0.6533 | 0.7903 and 0.6390 | 0.8420 and 0.6900 | 0.7414 and 0.4950 |
| no. of data/restraints/params | 10390 / 0 / 421 | 10647 / 89 / 420 | 6322 / 0 / 251 | 3080 / 7 / 136 |
| final *R* indices [$I>2\sigma(I)$] [a, b] | R1 = 0.0436, wR2 = 0.0629 | R1 = 0.0699, wR2 = 0.0758 | R1 = 0.0340, wR2 = 0.0817 | R1 = 0.0652, wR2 = 0.1329 |
| *R* indices (all data) | R1 = 0.0828, wR2 = 0.0664 | R1 = 0.1735, wR2 = 0.0919 | R1 = 0.0400, wR2 = 0.0856 | R1 = 0.0670, wR2 = 0.1336 |
| goodness-of-fit on F$^2$ [c] | 1.011 | 0.920 | 1.038 | 1.368 |
| large diff peak and hole, e Å$^{-3}$ | 1.170 and –0.601 | 2.413 and –2.120 | 0.639 and –0.555 | 1.497 and –1.663 |

[a] $R = (\Sigma||F_o| - |F_c||)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. [c] $\mathrm{GoF} = [(\Sigma\omega|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$

| complexes | **2.29** | **2.30** | **2.31** | **2.32** |
|---|---|---|---|---|
| formula | $C_{28}H_{46}I_6Ru_2S_6$ | $C_{29}H_{49}IRu_2S_6$ | $C_{15}H_{26}RuS_3$ | $C_{27}H_{53}F_6PRuS_3Sn$ |
| $M_r$ | 1538.55 | 919.08 | 403.61 | 838.60 |
| temp, K | 297(2) | 223(2) | 223(2) | 223(2) |
| cryst color and habit | dark brown, orthorhombic | dark red, needle | orange, orthorhombic | orange, cuboid |
| cryst size, mm | 0.35 × 0.18 × 0.10 | 0.11 × 0.08 × 0.04 | 0.40 × 0.30 × 0.10 | 0.40 × 0.40 × 0.26 |
| cryst system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| space group | $P2_1/n$ | $P2_1/n$ | Cm | $P2_1/c$ |
| $a$, Å | 12.0847(8) | 11.7001(11) | 8.940(2) | 11.143(4) |
| $b$, Å | 13.1360(9) | 21.831(2) | 14.049(3) | 25.756(8) |
| $c$, Å | 14.0009(10) | 14.0132(14) | 8.0857(18) | 12.561(4) |
| $\alpha$, deg | 90 | 90 | 90 | 90 |
| $\beta$, deg | 103.237(2) | 106.323(2) | 122.452(4) | 100.160(8) |
| $\gamma$, deg | 90 | 90 | 90 | 90 |
| $V$, Å$^3$ | 2163.5(3) | 3435.0(6) | 857.0(3) | 3548(2) |
| $Z$ | 2 | 4 | 2 | 4 |
| density, g cm$^{-3}$ | 2.362 | 1.777 | 1.564 | 1.570 |
| abs. coeff, mm$^{-1}$ | 5.288 | 2.162 | 1.266 | 1.399 |
| $F$(000) | 1432 | 1840 | 416 | 1704 |
| $\theta$ range for data collection | 2.01 to 30.10 | 2.01 to 25.35 | 2.90 to 27.49 | 1.58 to 27.49 |
| index ranges | –17<=h<=16, –12<=k<=18, –19<=l<=19 | –14<=h<=13, 0<=k<=26, 0<=l<=16 | –11<=h<=11, –17<=k<=18, –10<=l<=10 | –14<=h<=14, –32<=k<=33, –10<=l<=16 |
| no. of reflns collected | 17207 | 43751 | 2931 | 24606 |
| indep reflns | 6172 | 6284 | 1567 | 8134 |
| max. and min. transmission | 1.0000 and 0.6409 | 0.9185 and 0.7969 | 0.8838 and 0.6314 | 0.7125 and 0.6046 |
| no. of data/restraints/params | 6172 / 3 / 204 | 6284 / 64 / 352 | 1567 / 2 / 126 | 8134 / 48 / 379 |
| final $R$ indices [$I>2\sigma(I)$] [a, b] | R1 = 0.0577, wR2 = 0.1392 | R1 = 0.1119, wR2 = 0.2191 | R1 = 0.0332, wR2 = 0.0720 | R1 = 0.0529, wR2 = 0.1320 |
| $R$ indices (all data) | R1 = 0.0781, wR2 = 0.1506 | R1 = 0.1352, wR2 = 0.2284 | R1 = 0.0346, wR2 = 0.0730 | R1 = 0.0629, wR2 = 0.1381 |
| goodness-of-fit on F$^2$ [c] | 1.044 | 1.333 | 1.027 | 1.082 |
| large diff peak and hole, e Å$^{-3}$ | 2.318 and –1.258 | 2.169 and –1.683 | 0.772 and –0.328 | 1.860 and –0.457 |

[a] $R = (\Sigma||F_o| - |F_c||)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega||F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. [c] $\mathrm{GoF} = [(\Sigma\omega||F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$

| complexes | **2.33** | **2.34** | **2.35** | **2.36** |
|---|---|---|---|---|
| formula | $C_{14}H_{24}NRuS_2$ | $C_{34}H_{60}F_{12}N_4P_2Ru_2S_4$ | $C_{31}H_{54}Cl_4F_6NPRu_2S_5$ | $C_{18}H_{30}N_2RuS_2$ |
| $M_r$ | 371.53 | 1145.18 | 1089.96 | 439.63 |
| temp, K | 223(2) | 223(2) | 223(2) | 223(2) |
| cryst color and habit | dark purple, needle | dark red, orthorhombic | dark brown, orthorhombic | red, cuboid |
| cryst size, mm | 0.30 × 0.10 × 0.04 | 0.04 × 0.12 × 0.20 | 0.24 × 0.20 × 0.04 | 0.30 × 0.26 × 0.12 |
| cryst system | Orthorhombic | Triclinic | Triclinic | Orthorhombic |
| space group | Pbca | P $\bar{1}$ | P $\bar{1}$ | P2(1)2(1)2(1) |
| *a*, Å | 9.9108(6) | 10.2936(5) | 11.692(7) | 9.7421(7) |
| *b*, Å | 16.7046(10) | 11.5407(6) | 13.434(8) | 11.9068(8) |
| *c*, Å | 18.7762(11) | 12.1641(6) | 15.894(9) | 16.4702(11) |
| $\alpha$, deg | 90 | 63.234(1) | 75.722(8) | 90 |
| $\beta$, deg | 90 | 65.700(1) | 73.322(7) | 90 |
| $\gamma$, deg | 90 | 67.340(1) | 66.120(7) | 90 |
| *V*, Å$^3$ | 3108.5(3) | 1138.75(10) | 2162(2) | 1910.5(2) |
| *Z* | 8 | 1 | 2 | 4 |
| density, g cm$^{-3}$ | 1.588 | 1.670 | 1.674 | 1.528 |
| abs. coeff, mm$^{-1}$ | 1.261 | 0.997 | 1.275 | 1.040 |
| *F*(000) | 1528 | 582 | 1104 | 912 |
| $\theta$ range for data collection | 2.17 to 27.49 | 1.96 to 27.50 | 1.68 to 22.50 | 2.11 to 30.05 |
| index ranges | –12<=h<=12, –14<=k<=21, –24<=l<=24 | –13<=h<=13, –14<=k<=14, –15<=l<=15 | –12<=h<=12, –14<=k<=14, –17<=l<=17 | –13<=h<=12, –16<=k<=16, –19<=l<=22 |
| no. of reflns collected | 20632 | 14978 | 14890 | 15629 |
| indep reflns | 3569 | 5222 | 5660 | 5402 |
| max. and min. transmission | 0.9513 and 0.7035 | 0.9612 and 0.8255 | 0.9508 and 0.7496 | 0.863713 and 0.665252 |
| no. of data/restraints/params | 3569 / 0 / 259 | 5222 / 0 / 273 | 5660 / 64 / 478 | 5402 / 0 / 219 |
| final *R* indices [$I>2\sigma(I)$] [a, b] | R1 = 0.0556, wR2 = 0.1049 | R1 = 0.0417, wR2 = 0.0970 | R1 = 0.0931, wR2 = 0.2083 | R1 = 0.0377, wR2 = 0.0845 |
| *R* indices (all data) | R1 = 0.0701, wR2 = 0.1101 | R1 = 0.0471, wR2 = 0.0998 | R1 = 0.1483, wR2 = 0.2309 | R1 = 0.0408, wR2 = 0.0859 |
| goodness-of-fit on F$^2$ [c] | 1.217 | 1.091 | 1.063 | 1.080 |
| large diff peak and hole, e Å$^{-3}$ | 0.979 and –1.636 | 0.957 and –0.603 | 1.550 and –1.082 | 0.894 and –0.688 |

[a] $R = (\Sigma||F_o| - |F_c||)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega||F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. [c] $\mathrm{GoF} = [(\Sigma\omega||F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$

| complexes | **2.37** | **2.39** | **2.40** | **2.41** |
|---|---|---|---|---|
| formula | $C_{19}H_{34}F_{12}N_2O_2P_2RuS_2$ | $C_{22}H_{41}F_{12}N_3O_4P_2RuS_2$ | $C_{19}H_{36}F_6IN_2O_2PRuS_2$ | $C_{19}H_{32}F_6NPRuS_2$ |
| $M_r$ | 777.61 | 866.71 | 761.56 | 584.62 |
| temp, K | 223(2) | 223(2) | 223(2) | 293(2) |
| cryst color and habit | yellow, needle | yellow, orthorhombic | yellow, orthorhombic | red, orthorhombic |
| cryst size, mm | 0.14 × 0.12 × 0.10 | 0.50 × 0.40 × 0.24 | 0.38 × 0.10 × 0.04 | 0.20 × 0.18 × 0.08 |
| cryst system | Orthorhombic | Triclinic | Orthorhombic | Orthorhombic |
| space group | Pna2(1) | P-1 | Pbca | Pbca |
| *a*, Å | 17.7539(11) | 10.1429(5) | 16.9370(10) | 10.0476(5) |
| *b*, Å | 11.8517(8) | 10.6403(5) | 16.8727(10) | 18.5151(9) |
| *c*, Å | 13.7702(9) | 16.5359(8) | 19.7224(12) | 24.9301(12) |
| $\alpha$, deg | 90 | 108.210(1) | 90 | 90 |
| $\beta$, deg | 90 | 98.132(1) | 90 | 90 |
| $\gamma$, deg | 90 | 93.963(1) | 90 | 90 |
| *V*, Å$^3$ | 2897.4(3) | 1665.96(14) | 5636.1(6) | 4637.8(4) |
| *Z* | 4 | 2 | 8 | 8 |
| density, g cm$^{-3}$ | 1.783 | 1.728 | 1.795 | 1.675 |
| abs. coeff, mm$^{-1}$ | 0.895 | 0.793 | 1.916 | 0.980 |
| *F*(000) | 1568 | 880 | 3024 | 2384 |
| $\theta$ range for data collection | 2.07 to 27.49 | 2.03 to 27.50 | 1.99 to 25.00 | 1.63 to 27.50 |
| index ranges | –22<=h<=23, –15<=k<=15, –17<=l<=12 | –13<=h<=13, –13<=k<=13, –21<=l<=21 | –20<=h<=15, –19<=k<=20, –23<=l<=23 | –13<=h<=9, –13<=k<=23, –32<=l<=29 |
| no. of reflns collected | 19349 | 21453 | 30654 | 31086 |
| indep reflns | 5086 | 7632 | 4948 | 5321 |
| max. and min. transmission | 0.9158 and 0.8849 | 0.8324 and 0.6924 | 0.9273 and 0.5297 | 0.9257 and 0.8281 |
| no. of data/restraints/params | 5086 / 653 / 354 | 7632 / 694 / 604 | 4948 / 18 / 320 | 5321 / 0 / 405 |
| final *R* indices [$I>2\sigma(I)$] [a, b] | R1 = 0.0475, wR2 = 0.1294 | R1 = 0.0322, wR2 = 0.0885 | R1 = 0.0583, wR2 = 0.1151 | R1 = 0.0493, wR2 = 0.0992 |
| *R* indices (all data) | R1 = 0.0515, wR2 = 0.1330 | R1 = 0.0337, wR2 = 0.0897 | R1 = 0.0774, wR2 = 0.1221 | R1 = 0.0611, wR2 = 0.1033 |
| goodness-of-fit on F$^2$ [c] | 1.038 | 1.035 | 1.138 | 1.197 |
| large diff peak and hole, e Å$^{-3}$ | 0.838 and –0.548 | 0.629 and –0.592 | 0.809 and –1.230 | 1.037 and –1.098 |

[a] $R = (\Sigma||F_o| - |F_c||)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega||F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. [c] $\mathrm{GoF} = [(\Sigma\omega||F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$

| complexes | **2.42** | **2.43** | **2.44** |
|---|---|---|---|
| formula | $C_{22}H_{37}BrF_6N_1PRuS_2${1.83($CH_3CN$)} | $C_{20}H_{34}F_6NPRuS_2$ | $C_{18}H_{30}F_6NPRuS_2$ |
| $M_r$ | 779.85 | 598.64 | 570.59 |
| temp, K | 223(2) | 223(2) | 223(2) |
| cryst color and habit | yellow, hexagonal | red, orthorhombic | red, cuboid |
| cryst size, mm | 0.36 × 0.20 × 0.10 | 0.20 × 0.14 × 0.12 | 0.46 × 0.36 × 0.22 |
| cryst system | Hexagonal | Monoclinic | Monoclinic |
| space group | P6(3)/m | P2(1)/c | P2(1)/n |
| $a$, Å | 16.7659(5) | 8.9741(5) | 12.3846(7) |
| $b$, Å | 16.7659(5) | 16.8112(9) | 13.8429(7) |
| $c$, Å | 45.705(3) | 15.8708(8) | 13.7618(8) |
| $\alpha$, deg | 90 | 90 | 90 |
| $\beta$, deg | 90 | 92.5870(10) | 107.0470(10) |
| $\gamma$, deg | 120 | 90 | 90 |
| $V$, Å$^3$ | 11126.3(8) | 2391.9(2) | 2255.6(2) |
| $Z$ | 12 | 4 | 4 |
| density, g cm$^{-3}$ | 1.795 | 1.662 | 1.680 |
| abs. coeff, mm$^{-1}$ | 1.704 | 0.952 | 1.005 |
| $F$(000) | 4744 | 1224 | 1160 |
| $\theta$ range for data collection | 1.66 to 24.00 | 1.77 to 27.50 | 1.95 to 30.01 |
| index ranges | –17<=h<=19, –19<=k<=17, –46<=l<=52 | –11<=h<=7, –21<=k<=21, –20<=l<=20 | –14<=h<=17, –13<=k<=19, –18<=l<=19 |
| no. of reflns collected | 59241 | 16640 | 18088 |
| indep reflns | 5914 | 5492 | 6408 |
| max. and min. transmission | 0.8481 and 0.5790 | 0.8943 and 0.8324 | 0.8091 and 0.6549 |
| no. of data/restraints/params | 5914 / 102 / 373 | 5492 / 13 / 314 | 6408 / 357 / 326 |
| final $R$ indices [$I>2\sigma(I)$] [a, b] | R1 = 0.1325, wR2 = 0.3183 | R1 = 0.0399, wR2 = 0.0956 | R1 = 0.0367, wR2 = 0.0904 |
| $R$ indices (all data) | R1 = 0.1637, wR2 = 0.3342 | R1 = 0.0505, wR2 = 0.1000 | R1 = 0.0437, wR2 = 0.0944 |
| goodness-of-fit on F$^2$ [c] | 1.102 | 1.042 | 1.043 |
| large diff peak and hole, e Å$^{-3}$ | 2.360 and –1.613 | 0.909 and –403 | 0.926 and –0.310 |

[a] $R = (\Sigma||F_o| - |F_c||)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega||F_o| - |F_c||)^2/\Sigma\omega|F_o|^2]^{1/2}$. [c] $\mathrm{GoF} = [(\Sigma\omega||F_o| - |F_c||)^2/(N_{obs} - N_{param})]^{1/2}$

| complexes | **2.45** | **2.46** |
|---|---|---|
| formula | $C_{18.50}H_{31.50}F_6N_{1.50}OPRuS_2$ | $C_{20}H_{33.50}F_6N_{1.50}PRuS_2$ |
| $M_r$ | 601.11 | 605.14 |
| temp, K | 223(2) | 223(2) |
| cryst color and habit | orange, orthorhombic | orange, orthorhombic |
| cryst size, mm | 0.15 × 0.12 × 0.10 | 0.30 × 0.18 × 0.14 |
| cryst system | Monoclinic | Monoclinic |
| space group | P2(1)/c | P2(1)/c |
| *a*, Å | 17.947(3) | 18.3830(9) |
| *b*, Å | 21.283(4) | 21.1216(11) |
| *c*, Å | 12.559(2) | 12.5607(6) |
| $\alpha$, deg | 90 | 90 |
| $\beta$, deg | 102.396(4) | 101.832(1) |
| $\gamma$, deg | 90 | 90 |
| *V*, Å$^3$ | 4685.5(14) | 4773.4(4) |
| *Z* | 8 | 8 |
| density, g cm$^{-3}$ | 1.704 | 1.684 |
| abs. coeff, mm$^{-1}$ | 0.976 | 0.956 |
| *F*(000) | 2448 | 2472 |
| $\theta$ range for data collection | 1.50 to 25.00 | 1.13 to 25.00 |
| index ranges | –21<=h<=10, –25<=k<=25, –14<=l<=14 | –21<=h<=21, –25<=k<=25, –14<=l<=14 |
| no. of reflns collected | 25908 | 27372 |
| indep reflns | 8258 | 8382 |
| max. and min. transmission | 0.9087 and 0.8674 | 0.8778 and 0.7625 |
| no. of data/restraints/params | 8258 / 771 / 616 | 8382 / 2 / 599 |
| final *R* indices [$I>2\sigma(I)$] [a, b] | R1 = 0.0737, wR2 = 0.1424 | R1 = 0.0558, wR2 = 0.1189 |
| *R* indices (all data) | R1 = 0.1236, wR2 = 0.1585 | R1 = 0.0739, wR2 = 0.1309 |
| goodness-of-fit on F$^2$ [c] | 1.059 | 1.092 |
| large diff peak and hole, e Å$^{-3}$ | 1.416 and –1.052 | 0.919 and –653 |

[a] $R = (\Sigma||F_o| - |F_c||)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega||F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$.

[c] $\mathrm{GoF} = [(\Sigma\omega||F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$