Supplementary material for the manuscript

# Co(III) Complexes of the Pentadentate NHC ligand PY4Im: Carbene-Induced *Trans* Influences and the Non-Disappearing $^{13}C$ NMR Peak.

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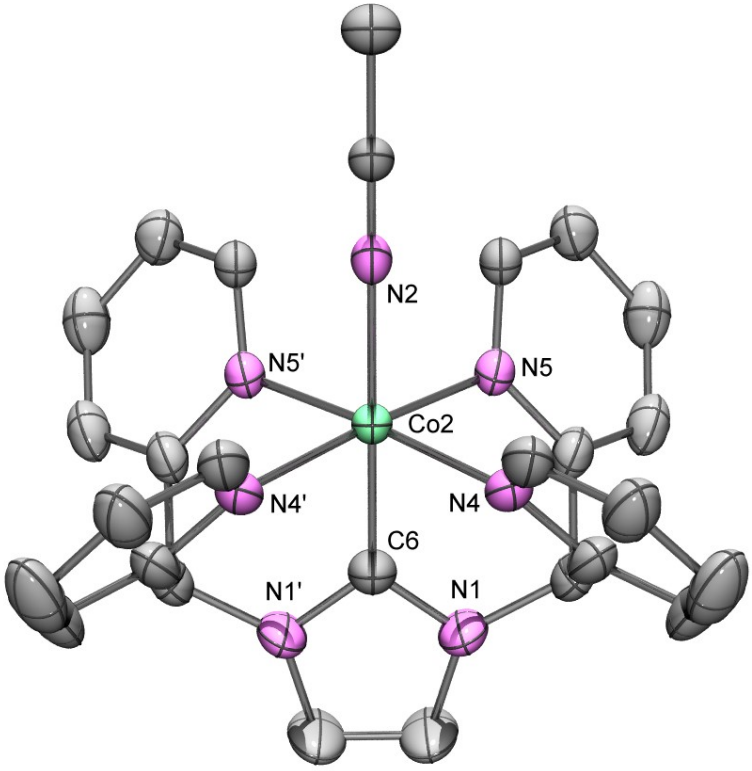



**Figure S1.** Structure of the $[(PY4Im)Co(NCMe)]^{3+}$ cation. The C-H hydrogen atoms have been removed for clarity. Bond lengths (Å) and angles (°): Co(2)-N(2) 1.951(3), Co(2)-N(5) 1.991(2), Co(2)-N4 1.999(2), Co(2)-C(6) 1.835(4); N(2)-Co(2)-N(5) 92.45(8), N(2)-Co(2)-N(4) 92.43(8), N(5)-Co(2)-N(5') 95.21(11), N(5)-Co(2)-N(4) 83.84(8), N(5)-Co(2)-N(4') 175.07(9), N(4)-Co2-N(4') 96.70(12), C(6)-Co(2)-N(2) 179.74(17), C(6)-Co(2)-N(5) 87.73(11), C(6)-Co(2)-N(4) 87.40(12).

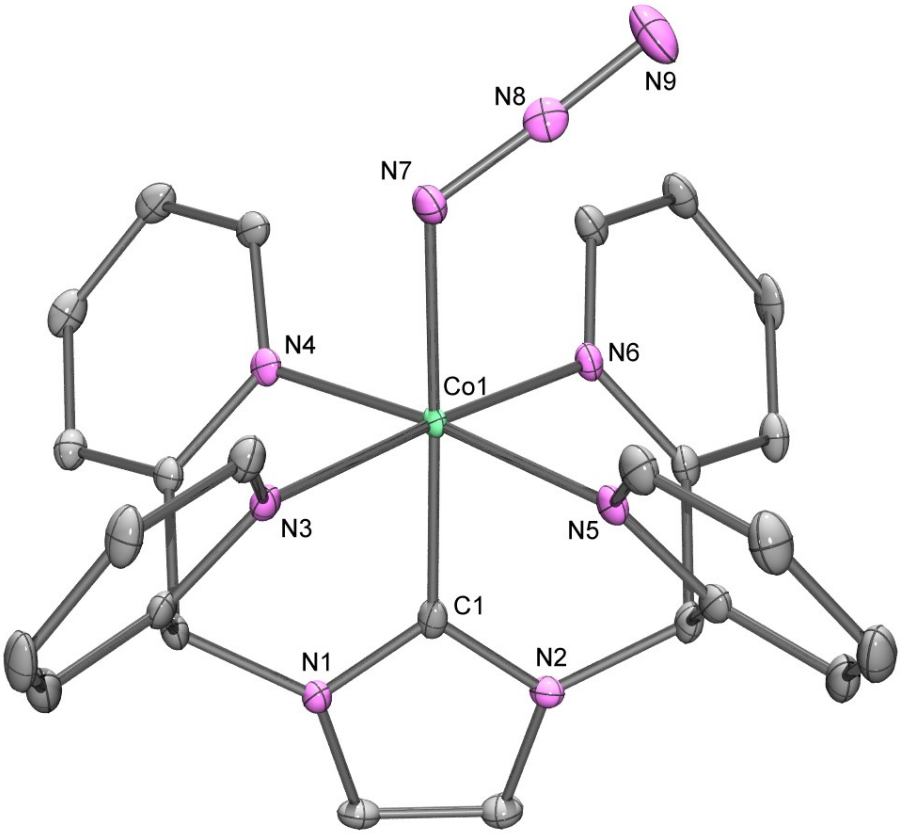



**Figure S2.** Structure of the $[(PY4Im)Co(N_3)]^{2+}$ cation. The C-H hydrogen atoms have been removed for clarity. Bond lengths (Å) and angles (°): Co(1)-C(1) 1.862(2), Co(1)-N(7) 1.9708(18), Co(1)-N(3) 1.9812(18), Co(1)-N(5) 1.9899(18), Co(1)-N(6), 1.9968(17), Co(1)-N(4) 2.0164(18), N(8)-N(9) 1.155(3), N(8)-N(7) 1.210(3); C(1)-Co(1)-N(7) 177.68(8), C(1)-Co(1)-N(3) 87.53(8), N(7)-Co(1)-N(3) 90.16(7), C(1)-Co(1)-N(5) 86.44(8), N(7)-Co(1)-N(5) 93.84(8), N(3)-Co(1)-N(5) 96.77(7), C(1)-Co(1)-N(6) 88.05(8), N(7)-Co(1)-N(6) 94.27(7), N(3)-Co(1)-N(6) 175.48(7), N(5)-Co(1)-N(6) 83.89(7), C(1)-Co(1)-N(4) 87.34(8), N(7)-Co(1)-N(4) 92.37(8), N(3)-Co(1)-N(4) 82.70(7), N(5)-Co(1)-N(4) 173.77(7), N(6)-Co(1)-N(4) 96.16(7), N(9)-N(8)-N(7) 177.7(2), N(8)-N(7)-Co(1) 119.48(14).

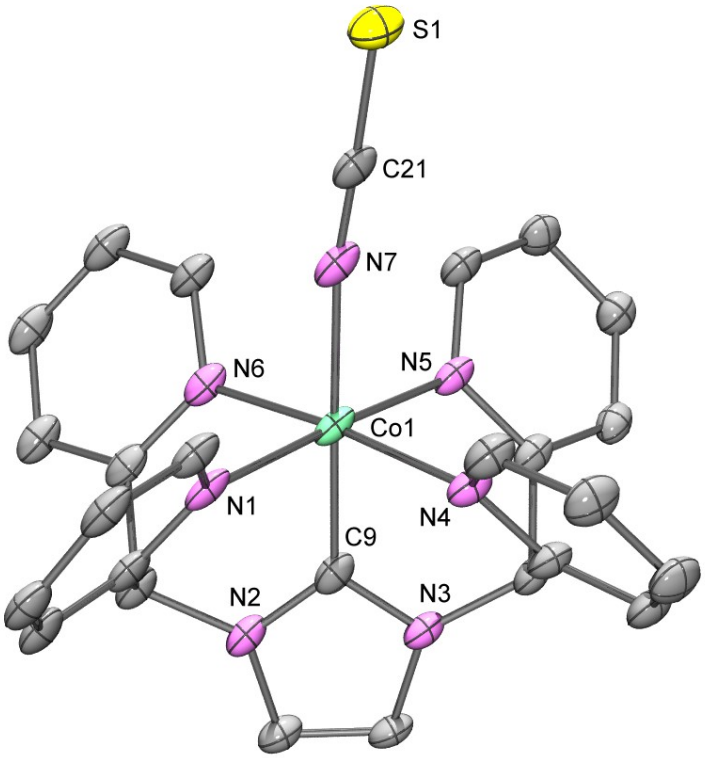



**Figure S3.** Structure of the $[(PY4Im)Co(NCS)]^{2+}$ cation. The C-H hydrogen atoms have been removed for clarity. Bond lengths (Å) and angles (°): Co(1)-N1 1.981(2), Co(1)-N(4) 2.000(2), Co(1)-N(5) 1.994(2), Co(1)-N(6) 1.999(2), Co(1)-N(7) 1.931(2), Co(1)-C(9) 1.841(3); N(1)-Co(1)-N(4) 96.41(9), N(1)-Co(1)-N(5) 176.29(9), N(1)-Co(1)-N(6) 82.60(9), N(5)-Co(1)-N(4) 83.69(9), N(5)-Co(1)-N6 96.94(9) N(6)-Co(1)-N(4) 174.40(9), N(7)-Co(1)-N(1) 93.00(10), N(7)-Co(1)-N(4) 91.95(9), N(7)-Co(1)-N(5) 90.70(9), N(7)-Co(1)-N(6) 93.61(9), C(9)-Co(1)-N(1) 88.08(11), C(9)-Co(1)-N(4) 87.51(10), C(9)-Co(1)-N(5) 88.22(11), C(9)-Co(1)-N(6) 86.94(10), C(9)-Co(1)-N(7) 178.84(11) N(7)-C(21)-S(1) 178.1(3), C(21)-N(7)-Co(1) 170.6(2).

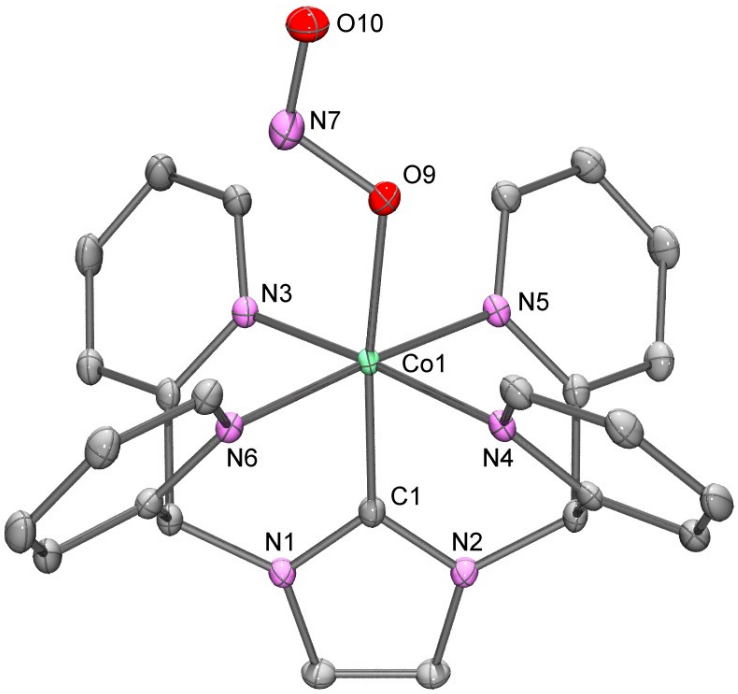



**Figure S4.** Structure of the $[(PY4Im)Co(ONO)]^{2+}$ cation. The C-H hydrogen atoms have been removed for clarity. Bond lengths (Å) and angles (°): Co(1)-C(1) 1.8452(19), Co(1)-O(9) 1.9404(13), Co(1)-N(4) 1.9864(15), Co(1)-N(5) 1.9910(15), Co(1)-N(3) 1.9920(16), Co(1)-N(6) 2.0023(15), O(9)-N(7) 1.314(2), O(10)-N(7) 1.222(2); C(1)-Co(1)-O(9) 173.53(7); C(1)-Co(1)-N(4) 87.28(7), O(9)-Co(1)-N(4) 87.28(6), C(1)-Co(1)-N(5) 87.63(7), O(9)-Co(1)-N(5) 88.26(6), N(4)-Co(1)-N(5) 83.22(6), C(1)-Co(1)-N(3) 88.15(7), O(9)-Co(1)-N(3) 97.23(6), N(4)-Co(1)-N(3) 175.31(6), N(5)-Co(1)-N(3) 95.57(6), C(1)-Co(1)-N(6) 87.67(7), O(9)-Co(1)-N(6) 96.55(6), N(4)-Co(1)-N(6) 98.03(6), N(5)-Co(1)-N(6) 175.07(6), N(3)-Co(1)-N(6) 82.80(6), N(7)-O(9)-Co(1) 119.52(11), O(10)-N(7)-O(9) 113.16(15).

**Table S1.** Crystal and refinement data for the $[(PY4Im)Co(X)]^{n+}$ complexes.

| | $[(PY4Im)Co(N_3)](ClO_4)_2.H_2O$ | $[(PY4Im)Co(NCMe)](ClO_4)_3.MeCN$ | $[(PY4Im)Co(OH)](ClO_4)_2.2.75H_2O$ | $[(PY4Im)Co(NCS)](ClO_4)_{1.5}(NCS)_{0.5}.2H_2O$ | $[(PY4Im)Co(ONO)](ClO_4)_2.1.5H_2O$ |
|---|---|---|---|---|---|
| Empirical formula | $C_{25}H_{22}Cl_2CoN_9O_9$ | $C_{29}H_{26}Cl_3CoN_8O_{12}$ | $C_{25}H_{26.5}Cl_2CoN_6O_{11.75}$ | $C_{26.50}H_{24}Cl_{1.50}CoN_{7.50}O_8S_{1.50}$ | $C_{25}H_{23}Cl_2CoN_7O_{11.50}$ |
| Formula weight | 722.34 | 843.86 | 728.85 | 735.73 | 735.33 |
| Temperature / K | 105(1) | 105.4(8) | 104(1) | 104(2) | 105.5(5) |
| Wavelength / Å | 1.54184 | 1.54184 | 1.54184 | 1.54184 | 1.54184 |
| Crystal system | Monoclinic | Orthorhombic | Triclinic | Monoclinic | Triclinic |
| Space group | C2/c | Pnma | P-1 | C2/c | P-1 |
| a / Å | 22.5235(3) | 16.1590(3) | 9.0704(2) | 12.4803(2) Å | 9.0838(2) |
| b / Å | 12.12400(10) | 17.8462(3) | 12.1819(3) | 24.2535(4) Å | 12.5241(2) |
| c / Å | 22.4083(3) | 13.1978(2) | 14.3572(3) | 19.8778(3) | 13.9453(2) |
| α / ° | 90 | 90 | 99.034(2) | 90 | 97.658(2) |
| β / ° | 116.387(2) | 90 | 105.917(2) | 104.524(2) | 108.587(2) |
| γ / ° | 90 | 90 | 107.125(2) | 90 | 107.640(2) |
| Volume / $Å^3$ | 5481.60(14) | 3805.94(11) | 1408.29(6) | 5824.55(17) | 1385.87(5) |
| Z | 8 | 4 | 2 | 8 | 2 |
| Density (calc) / Mg $m^{-3}$ | 1.751 | 1.473 | 1.719 | 1.678 | 1.762 |
| Absorp coeff / $mm^{-1}$ | 7.361 | 6.072 | 7.208 | 7.464 | 7.338 |
| F(000) | 2944 | 1720 | 747 | 3008 | 750 |
| Crystal size / $mm^3$ | 0.5 x 0.4 x 0.3 | 0.14 x 0.12 x 0.12 | 0.1 x 0.1 x 0.05 | 0.18 x 0.15 x 0.12 | 0.15 x 0.05 x 0.04 |
| Theta range | 4.254 to 72.371° | 4.166 to 72.452° | 3.931 to 72.390° | 3.645 to 67.725° | 3.458 to 72.468° |
| Index ranges | -17<=h<=27 | -19<=h<=19 | -11<=h<=8 | -14<=h<=11 | -11<=h<=10 |
| | -14<=k<=14 | -22<=k<=21 | -15<=k<=14 | -29<=k<=26 | -15<=k<=13 |
| | -27<=l<=26 | -11<=l<=16 | -17<=l<=17 | -21<=l<=23 | -15<=l<=17 |
| Reflections collected | 20952 | 17639 | 17589 | 24073 | 18024 |
| Independent reflections | 5213 [R(int) = 0.0359] | 3806 [R(int) = 0.0343] | 5283 [R(int) = 0.0519] | 5279 [R(int) = 0.0417] | 5271 [R(int) = 0.0282] |
| Completeness to θ = 67.684° / % | 99.3 | 99.9 | 98.1 | 99.8 | 99.8 |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Max and min transmission | 1.00000 and 0.35920 | 1.00000 and 0.78181 | 1.00000 and 0.49502 | 1.00000 and 0.65298 | 1.00000 and 0.80828 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 5213 / 0 / 424 | 3806 / 0 / 248 | 5283 / 29 / 443 | 5279 / 81 / 439 | 5271 / 0 / 435 |
| Goodness of fit on $F^2$ | 1.067 | 1.070 | 1.097 | 1.071 | 1.040 |
| Final R indices [I>2sigma(I)] | R1 = 0.0375, wR2 = 0.1040 | R1 = 0.0419, wR2 = 0.1161 | R1 = 0.0474, wR2 = 0.1247 | R1 = 0.0414, wR2 = 0.1047 | R1 = 0.0289, wR2 = 0.0725 |
| R indices (all data) | R1 = 0.0382, wR2 = 0.1046 | R1 = 0.0497, wR2 = 0.1214 | R1 = 0.0520, wR2 = 0.1271 | R1 = 0.0429, wR2 = 0.1058 | R1 = 0.0300, wR2 = 0.0731 |
| Extinction coefficient | 0.00024(3) | n/a | n/a | n/a | n/a |
| Largest diff. peak and hole | 0.623 and -0.750 e.$Å^{-3}$ | 0.281 and -0.377 e.$Å^{-3}$ | 1.041 and -0.937 e.$Å^{-3}$ | 0.720 and -0.607 e.$Å^{-3}$ | 0.456 and -0.403 e.$Å^{-3}$ |

| Complex cation | $[(PY4Im)Co(F)](ClO_4)_2.1.5H_2O$ | $[(PY4Im)Co(O_2CO)](ClO_4).2H_2O$ | $[(PY4Im)Co(N_3)_3].DMSO$ |
|---|---|---|---|
| Empirical formula | $C_{25}H_{23}Cl_2CoFN_6O_{9.50}$ | $C_{26}H_{24}ClCoN_6O_9$ | $C_{27}H_{27}CoN_{15}OS$ |
| Formula weight | 708.32 | 658.89 | 668.62 |
| Temperature / K | 120(1) | 104.5(9) | 120.0(4) |
| Wavelength / Å | 1.54184 | 1.54184 | 1.54184 |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | P-1 | P-1 | P-1 |
| a / Å | 12.7950(2) | 9.26770(10) | 13.4885(5) |
| b / Å | 14.1951(2) | 12.22350(10) | 15.3951(5) |
| c / Å | 16.8217(2) | 12.65450(10) | 16.3964(4) |
| α / ° | 105.4160(12) | 98.3430(10) | 89.394(2) |
| β / ° | 98.6806(12) | 110.8070(10) | 66.838(3) |
| γ / ° | 107.2355(14) | 92.9920(10) | 71.033(3) |
| Volume / $Å^3$ | 2724.15(7) | 1317.51(2) | 2933.38(18) |
| Z | 4 | 2 | 4 |
| Density (calc) / Mg $m^{-3}$ | 1.727 | 1.661 | 1.514 |
| Absorp coeff / $mm^{-1}$ | 7.425 | 6.644 | 5.688 |
| F(000) | 1444 | 676 | 1380 |
| Crystal size / $mm_3$ | 0.25 x 0.15 x 0.10 | 0.16 x 0.080 x 0.080 | 0.15 x 0.04 x 0.04 |
| Theta range | 2.814 to 72.449° | 3.678 to 72.479° | 2.958 to 72.959° |
| Index ranges | -15<=h<=15 | -11<=h<=11 | -15<=h<=16 |
| | -17<=k<=17 | -15<=k<=14 | -16<=k<=19 |
| | -20<=l<=20 | -15<=l<=15 | -20<=l<=20 |
| Reflections collected | 86489 | 16035 | 40399 |
| Independent reflections | 10434 [R(int) = 0.0354] | 4733 [R(int) = 0.0287] | 11274 [R(int) = 0.0756] |
| Completeness to θ = 67.684° / % | 99.9 | 99.4 | 99.8 |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Max and min transmission | 1.00000 and 0.65891 | 1.00000 and 0.78951 | 1.00000 and 0.74245 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 10434 / 42 / 840 | 4733 / 0 / 405 | 11274 / 74 / 819 |
| Goodness of fit on $F^2$ | 1.033 | 1.061 | 1.093 |
| Final R indices {I>2sigma(I)] | R1 = 0.0342, wR2 = 0.0869 | R1 = 0.0262, wR2 = 0.0685 | R1 = 0.0734, wR2 = 0.1925 |
| R indices (all data) | R1 = 0.0355, wR2 = 0.0876 | R1 = 0.0274, wR2 = 0.0689 | R1 = 0.0909, wR2 = 0.2049 |
| Extinction coefficient | 0.00022(4) | 0.00059(14) | 0.00056(15) |
| Largest diff. peak and hole | 1.096 and -0.690 e.$Å^{-3}$ | 0.306 and -0.329 e.$Å^{-3}$ | 2.423 and -1.023 e.$Å^{-3}$ |

**Computational Data**

The Cartesian coordinates of the optimized structures are listed below, along with their computed energies Geometries listed below were computed with M06 functionals using Gaussian 16. Underneath each set of coordinates are reported the number of imaginary frequencies, the electronic potential energy (E) and the Gibbs free energy at 298.15 K and 1 mol/L (G). All energies are given in Hartree.

**Table S2: $[(Py4Im)Co(OH)]^{2+}$**

Imaginary frequencies 0
E -1513.246168
G 298.15 K, 1 atm -1512.87334

| | | | |
|---|---|---|---|
| H | 0.835848 | -0.000132 | -2.770265 |
| Co | -0.000485 | 0.000014 | -0.551880 |
| N | 1.489523 | 1.329295 | -0.478917 |
| O | -0.070013 | -0.000164 | -2.447297 |
| N | 1.105699 | -0.000356 | 2.081435 |
| N | -1.503498 | 1.303697 | -0.456823 |
| C | 0.025271 | 0.000318 | 1.320356 |
| N | 1.489374 | -1.329482 | -0.478864 |
| N | -1.028406 | 0.000061 | 2.116758 |
| N | -1.503655 | -1.303589 | -0.456764 |
| C | -1.667421 | -2.241762 | -1.391496 |
| H | -0.984327 | -2.204954 | -2.229170 |
| C | 1.591792 | -2.323810 | -1.365753 |
| H | 0.856868 | -2.350970 | -2.157944 |
| C | -0.617232 | -0.000797 | 3.444652 |
| H | -1.315109 | -0.000936 | 4.266504 |
| C | -3.585899 | 3.118521 | -0.284414 |
| H | -4.394382 | 3.836886 | -0.206054 |
| C | -2.413659 | 1.208759 | 0.534413 |
| C | -2.688896 | 3.173219 | -1.334053 |
| H | -2.772684 | 3.916776 | -2.117158 |
| C | -2.689211 | -3.173047 | -1.333938 |
| H | -2.773074 | -3.916576 | -2.117063 |
| C | 2.442215 | 1.213941 | 0.469584 |
| C | 3.482870 | -2.113804 | 0.575814 |
| H | 4.223158 | -1.976346 | 1.355550 |
| C | -2.413775 | -1.208635 | 0.534507 |
| C | -2.316947 | 0.000089 | 1.438994 |
| H | -3.123669 | 0.000186 | 2.173538 |
| C | 3.559408 | 3.168617 | -0.320635 |
| H | 4.364188 | 3.891850 | -0.249925 |
| C | 2.442430 | -1.213898 | 0.469235 |
| C | -3.456496 | -2.103722 | 0.653337 |

| | | | |
|---|---|---|---|
| H | -4.163291 | -1.988994 | 1.467113 |
| C | -1.667151 | 2.241884 | -1.391562 |
| H | -0.984010 | 2.205028 | -2.229194 |
| C | 1.591994 | 2.323693 | -1.365734 |
| H | 0.857499 | 2.350461 | -2.158342 |
| C | -3.456358 | 2.103892 | 0.653164 |
| H | -4.163221 | 1.989191 | 1.466883 |
| C | 2.603982 | 3.265072 | -1.314146 |
| H | 2.632599 | 4.051434 | -2.058387 |
| C | 2.604240 | -3.264739 | -1.314806 |
| H | 2.632739 | -4.051061 | -2.059095 |
| C | 3.560216 | -3.167880 | -0.321873 |
| H | 4.365465 | -3.890646 | -0.251746 |
| C | 2.374817 | -0.000121 | 1.365816 |
| H | 3.201027 | -0.000160 | 2.077975 |
| C | -3.586142 | -3.118339 | -0.284242 |
| H | -4.394656 | -3.836664 | -0.205839 |
| C | 3.482156 | 2.114350 | 0.576833 |
| H | 4.222133 | 1.977105 | 1.356904 |
| C | 0.738416 | -0.001150 | 3.422073 |
| H | 1.463154 | -0.001820 | 4.220336 |

**Table S3: $[(Py4Im)Co(N_3)]^{2+}$**

Imaginary frequencies 0

E -1601.587679

G 298.15 K, 1 atm -1601.218281

| | | | |
|---|---|---|---|
| Co | -0.035835 | -0.000352 | -0.396443 |
| N | 1.438363 | -1.340788 | -0.177370 |
| N | -1.545501 | -1.315734 | -0.436107 |
| N | 1.151919 | -0.002448 | -2.902917 |
| N | -1.309297 | 0.000783 | 2.154272 |
| N | -1.545919 | 1.314700 | -0.437247 |
| N | 0.077937 | -0.000114 | -2.371755 |
| N | 0.819548 | 0.001119 | 2.317768 |
| N | 1.437796 | 1.341032 | -0.178865 |
| C | 1.621108 | -2.353658 | -1.032526 |
| H | 0.956739 | -2.417900 | -1.882209 |
| C | 1.620415 | 2.352638 | -1.035538 |
| H | 0.956389 | 2.415001 | -1.885655 |
| C | 0.328511 | 0.002707 | 3.617649 |
| H | 0.977676 | 0.003591 | 4.478408 |
| C | -1.623432 | -2.272380 | -1.365029 |
| H | -0.866735 | -2.271444 | -2.136960 |
| C | -2.648136 | -3.200769 | -1.392649 |
| H | -2.654915 | -3.956546 | -2.168383 |
| C | -3.644545 | -3.127509 | -0.438722 |
| H | -4.459969 | -3.842177 | -0.428910 |
| C | 2.304688 | -1.213177 | 0.850122 |
| C | -2.547493 | -1.209887 | 0.462256 |
| C | 2.303905 | 1.215185 | 0.848982 |
| N | 2.162388 | -0.004447 | -3.450219 |
| C | -3.601162 | 2.099554 | 0.490390 |
| H | -4.380285 | 1.970744 | 1.233068 |
| C | -0.185992 | 0.000096 | 1.461936 |
| C | 3.496592 | -3.170727 | 0.187526 |
| H | 4.296362 | -3.887322 | 0.336388 |
| C | -3.600925 | -2.099781 | 0.491782 |
| H | -4.380147 | -1.970439 | 1.234257 |
| C | -2.648549 | 3.199131 | -1.394956 |
| H | -2.655410 | 3.954366 | -2.171217 |
| C | 2.151334 | 0.001374 | 1.731210 |
| H | 2.901188 | 0.002006 | 2.523087 |
| C | -3.644812 | 3.126647 | -0.440810 |
| H | -4.460136 | 3.841437 | -0.431362 |
| C | -1.623932 | 2.270663 | -1.366866 |
| H | -0.867400 | 2.268910 | -2.138958 |
| C | -2.547775 | 1.209594 | 0.461315 |
| C | 3.494951 | 3.172473 | 0.184134 |
| H | 4.294265 | 3.889727 | 0.332289 |
| C | -2.531642 | 0.000212 | 1.366595 |
| H | -3.397718 | 0.000396 | 2.028136 |

| | | | |
|---|---|---|---|
| C | 2.628948 | -3.287349 | -0.881165 |
| H | 2.721250 | -4.084675 | -1.608134 |
| C | 2.627742 | 3.287046 | -0.885142 |
| H | 2.720025 | 4.083307 | -1.613279 |
| C | 3.333564 | 2.108941 | 1.057970 |
| H | 3.999522 | 1.959002 | 1.899708 |
| C | -1.023137 | 0.002418 | 3.513874 |
| H | -1.795820 | 0.003093 | 4.265802 |
| C | 3.334936 | -2.106055 | 1.059942 |
| H | 4.001051 | -1.954608 | 1.901289 |

**Table S4: [(Py4Im)Co(SCN)]$^{2+}$**

Imaginary frequencies 0

E -1928.451077

G 298.15 K, 1 atm -1928.08628

| | | | |
|---|---|---|---|
| Co | 0.013994 | 0.071195 | 0.165094 |
| S | -0.915774 | 2.090866 | 4.313478 |
| N | 1.511420 | 1.301186 | -0.338639 |
| N | 1.342156 | -0.996658 | -2.106478 |
| N | -0.782279 | -1.095896 | -2.297366 |
| N | -1.467836 | 1.169241 | -0.621499 |
| N | -1.466359 | -1.233278 | 0.516863 |
| N | 1.517031 | -1.096980 | 0.786905 |
| N | -0.194083 | 0.886755 | 1.896802 |
| C | 1.555598 | 2.570743 | 0.078417 |
| H | 0.774321 | 2.903935 | 0.746534 |
| C | 2.575901 | 3.433615 | -0.276972 |
| H | 2.554857 | 4.452503 | 0.088976 |
| C | 3.600923 | 2.968166 | -1.077973 |
| H | 4.412574 | 3.620890 | -1.378732 |
| C | 3.588081 | 1.637715 | -1.467985 |
| H | 4.386719 | 1.210133 | -2.062966 |
| C | 2.538243 | 0.833349 | -1.077969 |
| C | 2.548658 | -0.646017 | -1.375941 |
| H | 3.427903 | -0.916209 | -1.960718 |
| C | 1.088535 | -1.581087 | -3.340288 |
| H | 1.879717 | -1.891641 | -4.003244 |
| C | -0.259890 | -1.643657 | -3.461674 |
| H | -0.887981 | -2.020248 | -4.252686 |
| C | 0.201803 | -0.716506 | -1.503427 |
| C | -2.127578 | -0.860700 | -1.799526 |
| H | -2.857416 | -1.209073 | -2.529717 |
| C | -2.304212 | 0.612247 | -1.521968 |
| C | -3.335088 | 1.320518 | -2.103422 |
| H | -3.977329 | 0.824031 | -2.821596 |
| C | -3.529860 | 2.645946 | -1.746969 |
| H | -4.329801 | 3.223620 | -2.195991 |
| C | -2.700524 | 3.203678 | -0.793247 |
| H | -2.826928 | 4.223806 | -0.452757 |
| C | -1.689005 | 2.434246 | -0.248721 |
| H | -1.062403 | 2.844366 | 0.529740 |
| C | -2.304069 | -1.576341 | -0.483493 |
| C | -3.338368 | -2.470542 | -0.302414 |
| H | -3.980707 | -2.710225 | -1.142065 |
| C | -3.535373 | -3.030495 | 0.950466 |
| H | -4.337834 | -3.740610 | 1.114856 |
| C | -2.704805 | -2.645978 | 1.985581 |
| H | -2.833119 | -3.025133 | 2.991739 |
| C | -1.689978 | -1.741396 | 1.733408 |
| H | -1.062885 | -1.396655 | 2.542725 |

| | | | |
|---|---|---|---|
| C | -0.501665 | 1.391554 | 2.911131 |
| C | 2.547344 | -1.357793 | -0.044449 |
| C | 3.604638 | -2.161560 | 0.327655 |
| H | 4.407041 | -2.338887 | -0.378901 |
| C | 3.619595 | -2.712345 | 1.599995 |
| H | 4.437169 | -3.352428 | 1.911772 |
| C | 2.587786 | -2.406917 | 2.466483 |
| H | 2.566804 | -2.779174 | 3.483081 |
| C | 1.561433 | -1.590498 | 2.028468 |
| H | 0.774759 | -1.299387 | 2.709656 |

**Table S5: [(Py4Im)Co(ONO)]$^{2+}$**

Imaginary frequencies 0

E -1642.513005

G 298.15 K, 1 atm -1642.145771

| | | | |
|---|---|---|---|
| Co | -0.020364 | 0.000321 | -0.343703 |
| O | -0.053116 | 0.000637 | -2.291837 |
| N | -1.528372 | -1.311313 | -0.338237 |
| N | 0.928617 | -0.001367 | 2.334318 |
| C | 2.364460 | 1.212061 | 0.821019 |
| C | 0.479670 | -0.003294 | 3.648804 |
| H | 1.157118 | -0.004367 | 4.487443 |
| N | 1.459423 | 1.341894 | -0.171145 |
| N | -1.204690 | -0.000971 | 2.239558 |
| C | -0.874405 | -0.003082 | 3.588748 |
| H | -1.623118 | -0.003992 | 4.364430 |
| C | 2.241354 | -0.001173 | 1.707842 |
| H | 3.016240 | -0.001648 | 2.475707 |
| C | 3.540235 | 3.161087 | 0.107783 |
| H | 4.349058 | 3.873718 | 0.223166 |
| C | 2.630568 | 3.280802 | -0.924828 |
| H | 2.697002 | 4.076763 | -1.656119 |
| C | -0.103946 | -0.000081 | 1.511464 |
| C | 1.612860 | 2.351785 | -1.034728 |
| H | 0.915392 | 2.420815 | -1.856286 |
| C | 3.407223 | 2.099190 | 0.988314 |
| H | 4.105594 | 1.945358 | 1.802508 |
| C | -2.454539 | -0.000636 | 1.497491 |
| H | -3.296440 | -0.000913 | 2.190095 |
| O | 0.937563 | 0.003553 | -4.135977 |
| N | -1.528482 | 1.311619 | -0.337282 |
| N | 1.459327 | -1.341656 | -0.172801 |
| N | 1.072997 | 0.003222 | -2.934146 |
| C | -3.558735 | -2.092418 | 0.644485 |
| H | -4.313685 | -1.966699 | 1.412079 |
| C | 2.364258 | -1.213392 | 0.819647 |
| C | -2.502459 | -1.207633 | 0.590472 |
| C | -1.640544 | -2.257347 | -1.274911 |
| H | -0.905245 | -2.261669 | -2.066764 |
| C | 1.612856 | -2.350276 | -1.037884 |
| H | 0.915564 | -2.418008 | -1.859717 |
| C | 3.406820 | -2.100948 | 0.985908 |
| H | 4.105086 | -1.948347 | 1.800428 |
| C | -3.637646 | 3.109956 | -0.292433 |
| H | -4.456410 | 3.820197 | -0.263715 |
| C | -2.672638 | 3.179136 | -1.278265 |
| H | -2.708095 | 3.926779 | -2.060903 |
| C | -2.502419 | 1.207173 | 0.591522 |
| C | 2.630397 | -3.279612 | -0.929123 |
| H | 2.696882 | -4.074487 | -1.661588 |

| | | | |
|---|---|---|---|
| C | -3.637650 | -3.109603 | -0.295248 |
| H | -4.456427 | -3.819855 | -0.267229 |
| C | -2.672449 | -3.178029 | -1.280944 |
| H | -2.707747 | -3.925074 | -2.064161 |
| C | -1.640753 | 2.258418 | -1.273158 |
| H | -0.905687 | 2.263242 | -2.065220 |
| C | -3.558619 | 2.091994 | 0.646449 |
| H | -4.313427 | 1.965719 | 1.414097 |
| C | 3.539829 | -3.161605 | 0.103895 |
| H | 4.348484 | -3.874564 | 0.218438 |

**Table S6: [(Py4Im)Co(F)]$^{2+}$**

Imaginary frequencies 0

E -1537.291099

G 298.15 K, 1 atm -1536.930015

| | | | |
|---|---|---|---|
| Co | 0.000011 | 0.000083 | -0.516992 |
| F | -0.000043 | -0.000158 | -2.394448 |
| N | -1.488418 | -1.313816 | -0.433772 |
| N | 1.488571 | 1.313959 | -0.433845 |
| N | 1.490877 | -1.299140 | -0.470307 |
| N | -1.068248 | 0.019221 | 2.111288 |
| C | 1.633207 | -2.213352 | -1.432404 |
| H | 0.931680 | -2.164829 | -2.253628 |
| N | -1.491086 | 1.299163 | -0.470275 |
| C | 2.348373 | -0.023320 | 1.416622 |
| H | 3.164872 | -0.033877 | 2.139654 |
| N | 1.068728 | -0.018580 | 2.111109 |
| C | 1.617601 | 2.280862 | -1.344943 |
| H | 0.896462 | 2.296996 | -2.149429 |
| C | 0.000172 | 0.000102 | 1.335319 |
| C | -1.633781 | 2.213325 | -1.432353 |
| H | -0.932303 | 2.165216 | -2.253647 |
| C | 3.578654 | -3.110289 | -0.390266 |
| H | 4.389559 | -3.828933 | -0.347709 |
| C | 2.425532 | -1.221599 | 0.498100 |
| C | 0.678140 | -0.010221 | 3.444794 |
| H | 1.389888 | -0.020888 | 4.254513 |
| C | -1.617871 | -2.280352 | -1.345195 |
| H | -0.897086 | -2.296069 | -2.150019 |
| C | 2.645685 | 3.205534 | -1.301922 |
| H | 2.699080 | 3.972485 | -2.064767 |
| C | 2.432718 | 1.194388 | 0.522833 |
| C | -2.425662 | 1.221381 | 0.498196 |
| C | -2.347977 | 0.023284 | 1.416961 |
| H | -3.164396 | 0.033720 | 2.140089 |
| C | -3.472547 | 2.116036 | 0.572529 |
| H | -4.199383 | 2.015941 | 1.370522 |
| C | -0.677428 | 0.011293 | 3.444900 |
| H | -1.389024 | 0.022326 | 4.254748 |
| C | -3.585003 | -3.116407 | -0.292468 |
| H | -4.400149 | -3.828457 | -0.227444 |
| C | -2.432138 | -1.194567 | 0.523370 |
| C | 3.484293 | 2.080499 | 0.624352 |
| H | 4.217473 | 1.944290 | 1.410953 |
| C | 2.657144 | -3.143100 | -1.419759 |
| H | 2.724285 | -3.867673 | -2.221915 |
| C | -3.483417 | -2.080986 | 0.625304 |
| H | -4.216182 | -1.945169 | 1.412357 |
| C | 3.472033 | -2.116698 | 0.572487 |
| H | 4.198942 | -2.016840 | 1.370447 |

| | | | |
|---|---|---|---|
| C | -3.579624 | 3.109509 | -0.390289 |
| H | -4.390876 | 3.827763 | -0.347807 |
| C | -2.645823 | -3.205158 | -1.301921 |
| H | -2.699644 | -3.971738 | -2.065110 |
| C | 3.585552 | 3.116174 | -0.293165 |
| H | 4.400931 | 3.827985 | -0.228445 |
| C | -2.658090 | 3.142674 | -1.419750 |
| H | -2.725462 | 3.867210 | -2.221918 |

**Table S7: [(Py4Im)Co(OH$_2$)]$^{3+}$**

Imaginary frequencies 0

E -1513.706242

G 298.15 K, 1 atm -1513.320315

| | | | |
|---|---|---|---|
| Co | -0.000311 | -0.002243 | -0.532162 |
| O | -0.017012 | -0.167078 | -2.540492 |
| H | 0.663808 | 0.300417 | -3.041898 |
| H | -0.856958 | 0.019003 | -2.981438 |
| N | -1.064074 | 0.036554 | 2.085529 |
| N | 1.512672 | -1.313551 | -0.465440 |
| N | -1.491203 | -1.343937 | -0.409928 |
| N | 1.073041 | -0.003822 | 2.083132 |
| N | -1.510920 | 1.313624 | -0.474968 |
| N | 1.491609 | 1.345545 | -0.427240 |
| C | -2.438718 | -1.200112 | 0.540883 |
| C | 2.443825 | 1.210083 | 0.520116 |
| C | 2.448157 | -1.210285 | 0.500820 |
| C | 1.661484 | -2.265345 | -1.393605 |
| H | 0.956091 | -2.276787 | -2.211675 |
| C | 2.359325 | -0.008240 | 1.406142 |
| H | 3.163953 | -0.013114 | 2.142780 |
| C | -0.671241 | 0.029908 | 3.417327 |
| H | -1.384803 | 0.042976 | 4.225413 |
| C | -2.352430 | 0.028439 | 1.412490 |
| H | -3.154808 | 0.041847 | 2.151473 |
| C | 0.003696 | 0.014890 | 1.309896 |
| C | 2.623537 | 3.288559 | -1.227613 |
| H | 2.655353 | 4.087401 | -1.958021 |
| C | -3.486388 | -2.085809 | 0.673752 |
| H | -4.218720 | -1.923149 | 1.455800 |
| C | 3.502813 | -2.092811 | 0.599408 |
| H | 4.224642 | -1.965589 | 1.397738 |
| C | -2.690180 | 3.179894 | -1.379279 |
| H | -2.753804 | 3.924548 | -2.162912 |
| C | -1.607514 | -2.360684 | -1.271339 |
| H | -0.877233 | -2.428828 | -2.064841 |
| C | 2.695084 | -3.182957 | -1.356386 |
| H | 2.760239 | -3.932884 | -2.134934 |
| C | -1.657908 | 2.261060 | -1.408135 |
| H | -0.949498 | 2.275295 | -2.224939 |
| C | 1.601232 | 2.360117 | -1.292024 |
| H | 0.865697 | 2.427296 | -2.081048 |
| C | -2.445319 | 1.219761 | 0.493104 |
| C | -2.630934 | -3.287220 | -1.194429 |
| H | -2.668932 | -4.089793 | -1.920470 |
| C | 3.491152 | 2.098112 | 0.641656 |
| H | 4.227202 | 1.941676 | 1.421511 |
| C | -3.581007 | -3.157965 | -0.200273 |
| H | -4.393337 | -3.870243 | -0.110089 |

| | | | |
|---|---|---|---|
| C | 3.621662 | -3.110767 | -0.334532 |
| H | 4.439313 | -3.820074 | -0.272910 |
| C | 0.683463 | 0.007616 | 3.415792 |
| H | 1.398952 | -0.001593 | 4.222231 |
| C | 3.580326 | 3.165021 | -0.239175 |
| H | 4.392907 | 3.878104 | -0.158116 |
| C | -3.498583 | 2.104936 | 0.585107 |
| H | -4.219358 | 1.985883 | 1.385682 |
| C | -3.617152 | 3.115210 | -0.356999 |
| H | -4.434383 | 3.825429 | -0.300833 |

**Table S8: [(Py4Im)Co($CO_3$)]$^+$**

Imaginary frequencies 0

E -1701.362433

G 298.15 K, 1 atm -1700.991655

| | | | |
|---|---|---|---|
| Co | -0.360954 | 0.156426 | -0.566126 |
| N | 0.822039 | 0.106132 | 2.099806 |
| N | -1.531638 | -1.441463 | -0.685325 |
| C | 0.907932 | 2.639143 | -1.240235 |
| H | 0.180660 | 2.532067 | -2.033626 |
| C | -2.328548 | 2.319182 | -0.724305 |
| H | -1.632452 | 2.694681 | -1.462558 |
| C | 0.443294 | -0.148785 | 3.409170 |
| H | 1.127445 | -0.022487 | 4.233341 |
| C | -0.180137 | -0.163832 | 1.273911 |
| O | 1.087736 | -0.798326 | -1.353837 |
| O | -0.314019 | 0.370236 | -2.504918 |
| N | 0.944914 | 1.652224 | -0.331550 |
| C | 0.778276 | -0.347808 | -2.555444 |
| O | 1.425701 | -0.595261 | -3.565433 |
| C | 1.764269 | 3.721434 | -1.219656 |
| H | 1.672844 | 4.483200 | -1.984100 |
| C | 1.905953 | 1.695148 | 0.617511 |
| C | -3.276184 | -2.773434 | 0.253197 |
| H | -3.988820 | -2.914554 | 1.057982 |
| C | -2.436258 | -1.678459 | 0.281231 |
| C | 2.715090 | 3.795690 | -0.220359 |
| H | 3.399686 | 4.634304 | -0.158848 |
| C | -2.245362 | -3.425310 | -1.792739 |
| H | -2.129659 | -4.091200 | -2.638936 |
| C | -3.180836 | -3.665179 | -0.803224 |
| H | -3.826877 | -4.534839 | -0.848031 |
| C | 2.783165 | 2.764596 | 0.699644 |
| H | 3.527883 | 2.769114 | 1.488539 |
| C | -1.438177 | -2.307117 | -1.700987 |
| H | -0.703005 | -2.110825 | -2.469172 |
| N | -1.206197 | -0.552181 | 2.029095 |
| N | -2.013028 | 1.176985 | -0.107208 |
| C | -2.879919 | 0.667412 | 0.787328 |
| C | 2.915294 | -0.599477 | 1.029701 |
| C | 2.100894 | 0.559499 | 1.601048 |
| H | 2.647653 | 0.964616 | 2.460213 |
| C | -2.511375 | -0.665003 | 1.391118 |
| H | -3.249037 | -0.965985 | 2.135453 |
| C | -4.383160 | 2.489214 | 0.470648 |
| H | -5.308999 | 3.004214 | 0.701823 |
| C | -0.848540 | -0.545763 | 3.369559 |
| H | -1.536641 | -0.828826 | 4.149636 |
| C | -4.068759 | 1.294220 | 1.099985 |
| H | -4.732510 | 0.839902 | 1.826812 |

| | | | |
|---|---|---|---|
| C | -3.500051 | 3.004739 | -0.460122 |
| H | -3.705116 | 3.926983 | -0.989631 |
| C | 4.318475 | -2.709027 | 0.048375 |
| H | 4.837093 | -3.582788 | -0.329549 |
| C | 3.230149 | -2.852065 | 0.890819 |
| H | 2.895926 | -3.843544 | 1.188140 |
| C | 4.722157 | -1.425279 | -0.286106 |
| H | 5.576418 | -1.263340 | -0.935257 |
| N | 2.537460 | -1.822901 | 1.382962 |
| C | 4.012868 | -0.348073 | 0.215046 |
| H | 4.300017 | 0.667056 | -0.038475 |

**Table S9: [(Py4Im)Co($N_3$)$_3$]**

Imaginary frequencies 0

| | |
|---|---|
| E | -1930.196221 |
| G 298.15 K, 1 atm | -1929.815115 |

| | | | |
|---|---|---|---|
| Co | 1.195756 | 0.122541 | 0.680441 |
| N | 0.631210 | -0.434304 | -2.010857 |
| N | -1.269992 | -0.442001 | -1.031800 |
| N | 2.122319 | 1.445203 | -0.466156 |
| N | 2.488584 | -1.236882 | 0.019957 |
| N | -0.445732 | 1.476169 | 2.363610 |
| N | -0.917318 | 1.460321 | 3.412627 |
| N | 0.260040 | -1.176380 | 1.798068 |
| N | 2.306469 | 0.140782 | 3.243805 |
| N | 2.191246 | -0.287032 | 4.308768 |
| N | 0.149246 | -3.417693 | 1.107623 |
| N | 2.475304 | 0.593346 | 2.153230 |
| N | -0.008244 | 1.546191 | 1.252867 |
| C | 0.046243 | -0.273655 | -0.814975 |
| N | 0.210119 | -2.313418 | 1.420024 |
| C | 3.117647 | 3.579305 | -0.775541 |
| H | 3.354779 | 4.551415 | -0.360398 |
| C | 3.108371 | -2.079497 | 0.853321 |
| H | 2.850151 | -2.014331 | 1.904168 |
| C | -4.651745 | -0.739137 | -0.896623 |
| H | -4.763881 | 0.275386 | -1.265143 |
| C | 3.152163 | 1.976332 | -2.545903 |
| H | 3.412288 | 1.662654 | -3.550510 |
| C | 2.074634 | -0.278692 | -2.155735 |
| H | 2.336531 | -0.433204 | -3.203743 |
| C | 2.782356 | -1.283865 | -1.287510 |
| C | 2.466983 | 1.109761 | -1.717077 |
| C | 4.038789 | -2.999722 | 0.408634 |
| H | 4.512523 | -3.663202 | 1.121776 |
| C | -3.486879 | -1.134704 | -0.252177 |
| C | -2.321696 | -0.187428 | -0.042822 |
| H | -1.881199 | -0.436613 | 0.929273 |
| C | 3.483583 | 3.234398 | -2.065244 |
| H | 4.018418 | 3.937029 | -2.694931 |
| C | 2.436344 | 2.656754 | -0.002236 |
| H | 2.130785 | 2.873109 | 1.014113 |
| C | -0.304174 | -0.689002 | -2.998153 |
| H | -0.025988 | -0.848211 | -4.027597 |
| N | -3.304732 | -2.372745 | 0.215221 |
| C | -1.501264 | -0.686181 | -2.378991 |
| H | -2.494426 | -0.837946 | -2.771715 |
| C | 4.344873 | -3.047118 | -0.940752 |
| H | 5.071155 | -3.758151 | -1.318812 |
| C | 3.706759 | -2.170997 | -1.804422 |
| H | 3.912042 | -2.166639 | -2.868941 |

| | | | |
|---|---|---|---|
| C | -5.485856 | -2.952882 | -0.586816 |
| H | -6.252793 | -3.711797 | -0.693651 |
| C | -4.288383 | -3.253435 | 0.044517 |
| H | -4.114859 | -4.253208 | 0.436318 |
| C | -5.667541 | -1.667983 | -1.067815 |
| H | -6.587243 | -1.387577 | -1.570775 |
| N | -2.451394 | 2.031922 | -1.076177 |
| C | -2.728582 | 1.269919 | -0.022827 |
| C | -3.397055 | 1.741650 | 1.103349 |
| H | -3.601768 | 1.070814 | 1.933000 |
| C | -3.762201 | 3.073806 | 1.147645 |
| H | -4.270855 | 3.477302 | 2.017332 |
| C | -2.813629 | 3.316711 | -1.020629 |
| H | -2.570910 | 3.923054 | -1.890714 |
| C | -3.459718 | 3.885529 | 0.062234 |
| H | -3.720169 | 4.937969 | 0.052658 |

Table S10: Calculated and experimental $^{13}C$ chemical shifts for $[(Py4Im)Co(F)]^{2+}$

| **Calculated shifts / ppm** | **Experimental shifts / ppm** | **delta / ppm** |
|---|---|---|
| 201.04 | 158.0 (indirect) | 43.04 |
| 129.61 | 126.48 | 3.13 |
| 70.91 | 68.16 | 2.75 |
| 159.65 | 154.88 | 4.77 |
| 132.62 | 129.66 | 2.96 |
| 148.03 | 144.85 | 3.18 |
| 131.15 | 129.22 | 1.93 |
| 158.14 | 155.24 | 2.90 |

Table S11: Calculated and experimental $^{13}C$ chemical shifts for $[(Py4Im)Co(OH)]^{2+}$

| **Calculated shifts / ppm** | **Experimental shifts / ppm** | **delta** |
|---|---|---|
| 204.83 | 167.7 (indirect) | 37.13 |
| 128.87 | 122.70 | 6.17 |
| 70.92 | 65.28 | 5.64 |
| 160.26 | 152.47 | 7.79 |
| 132.46 | 126.15 | 6.31 |
| 147.55 | 141.17 | 6.38 |
| 130.89 | 125.64 | 5.25 |
| 158.91 | 153.23 | 5.68 |

Table S12: Calculated and experimental $^{13}C$ chemical shifts for $[(Py4Im)Co(OH_2)]^{3+}$

| **Calculated shifts / ppm** | **Experimental shifts / ppm** | **delta** |
|---|---|---|
| 196.19 | 155.4 | 40.79 |
| 155.83 | 152.72 | 3.10 |
| 128.21 | 126.68 | 1.53 |
| 145.43 | 142.45 | 2.98 |
| 128.15 | 127.35 | 0.80 |
| 161.46 | 151.72 | 9.74 |
| 65.58 | 65.39 | 0.19 |
| 130.24 | 123.98 | 6.26 |

Table S13: Calculated and experimental $^{13}C$ chemical shifts for $[(Py4Im)Co(NCS)]^{2+}$

| **Calculated shifts / ppm** | **Experimental shifts / ppm** | **delta** |
|---|---|---|
| 198.73 | 158.9 | 39.83 |
| 129.83 | 126.90 | 2.93 |
| 71.03 | 65.46 | 5.57 |
| 159.12 | 151.66 | 7.46 |
| 133.23 | 129.66 | 3.57 |
| 148.52 | 141.84 | 6.68 |
| 131.72 | 126.90 | 4.82 |
| 159.86 | 154.35 | 5.51 |

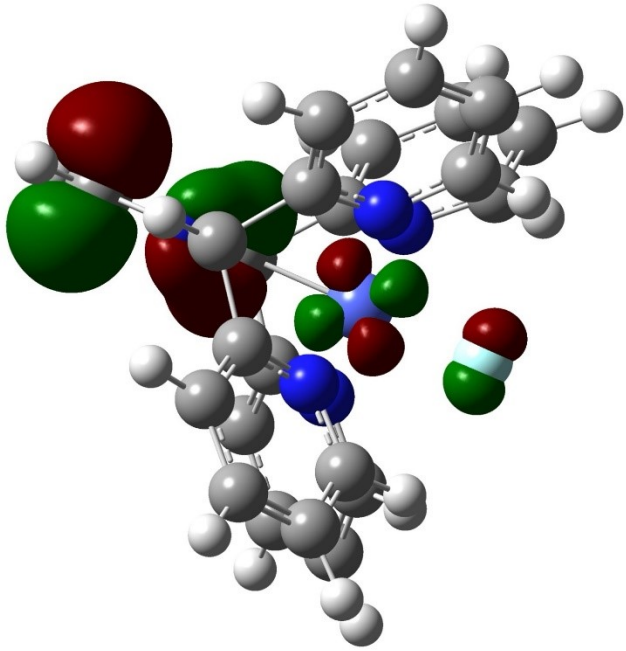
Table S14: Calculated and experimental $^{13}C$ chemical shifts for $[(Py4Im)Co(N_3)]^{2+}$

| **Calculated shifts / ppm** | **Experimental shifts / ppm** | **delta** |
|---|---|---|
| 202.8 | 163.02 | 39.78 |
| 128.86 | 126.08 | 2.78 |
| 64.98 | 68.41 | 3.43 |
| 161.56 | 155.03 | 6.53 |
| 128.15 | 129.82 | 1.67 |
| 144.99 | 144.67 | 0.32 |
| 129.2 | 129.54 | 0.34 |
| 157.72 | 156.79 | 0.93 |

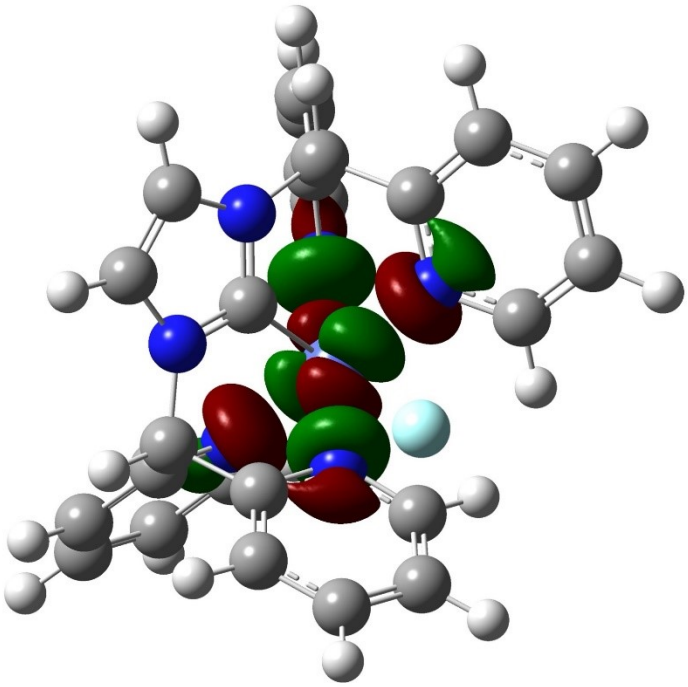
**Figure S5: Selected molecular orbitals of $[Co(PY4Im)Co(F)]^{2+}$ and $[Co(PY4Im)Co(N_3)]^{2+}$**

Fluorido complex Mayer bond order: C-0.879-Co-0.545-F

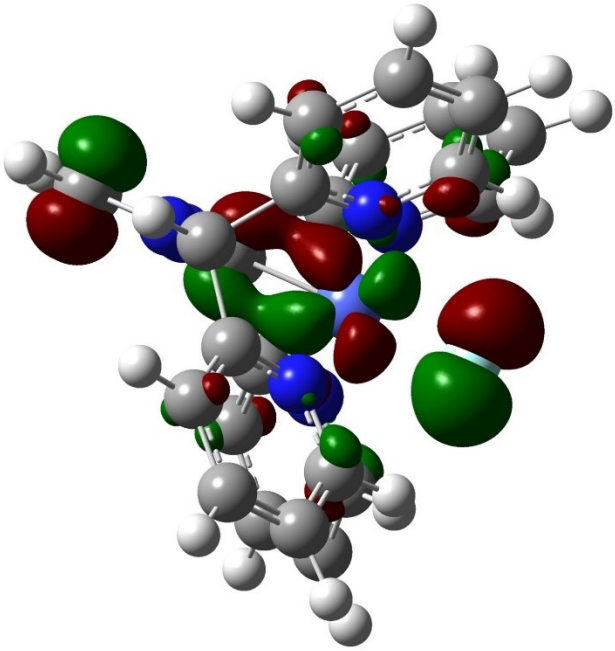
HOMO; Carbene C 14.9%, Co 14.2%, and F 3.30%



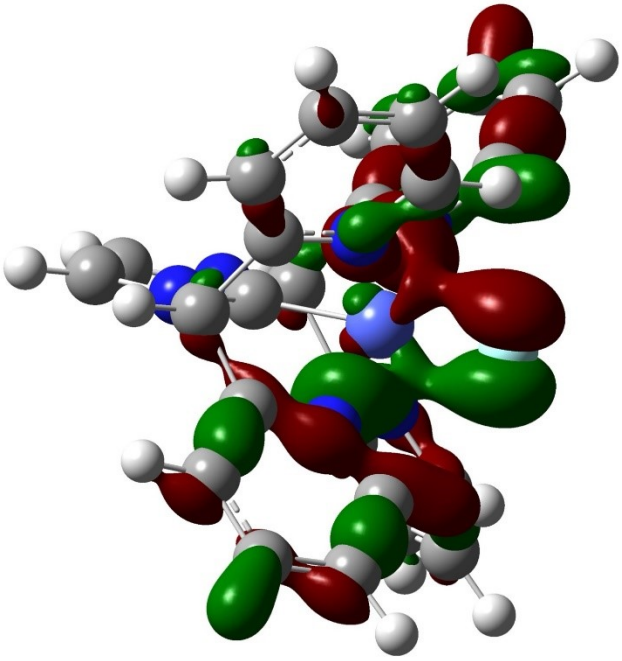
LUMO; Carbene 0.0160%, Co 61.5%, and F 0.00004%



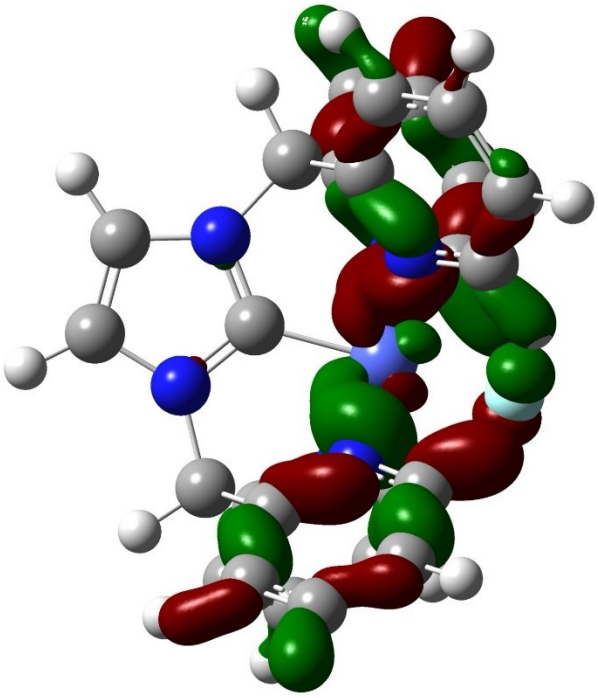
HOMO-7; π orbital between carbene 4.09% and Co 29.44% with an antibonding orbital between Co and F (26.8%)



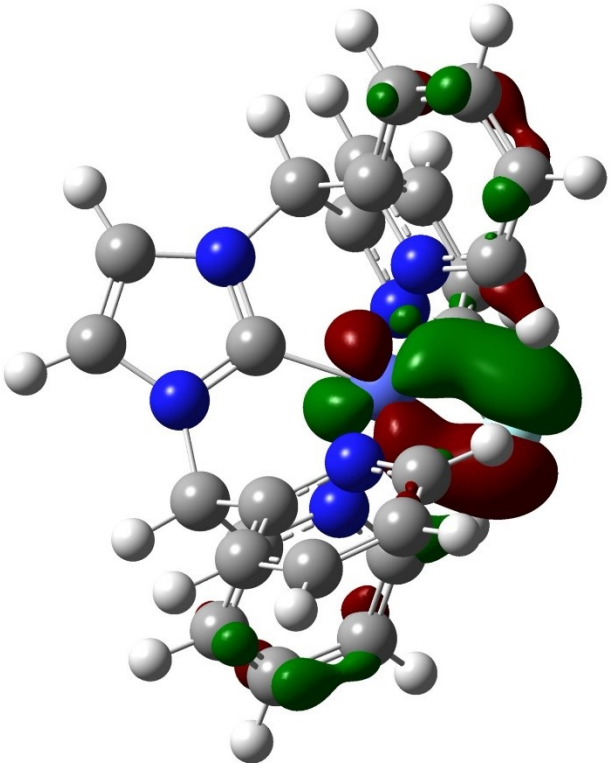
HOMO-13; mostly a bonding π orbital between Co (5.45%) and F (20.4%), Carbene (0.588%)



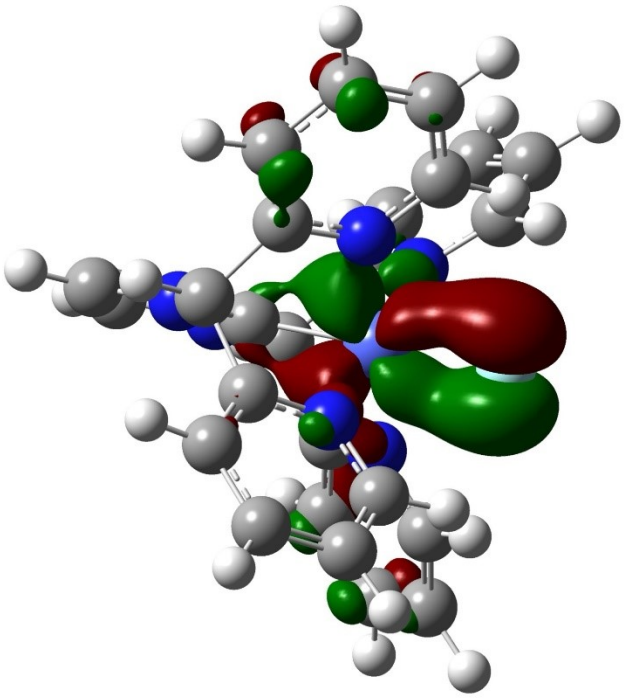
HOMO-14; very weak π bonding between Co (8.40%) and F (3.87%) and little on the carbene (0.243%)



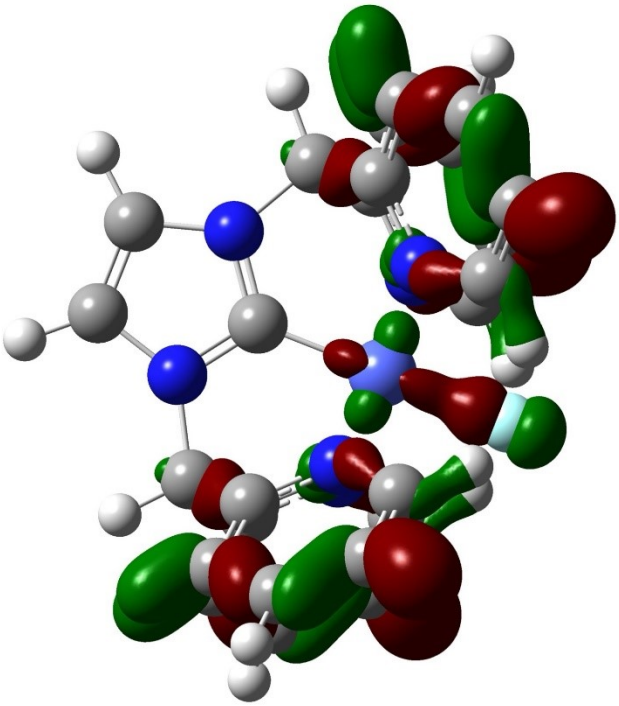
HOMO-16; significant π bonding Co (36.6%) and F (35.8%) and little on the carbene (0.449%)



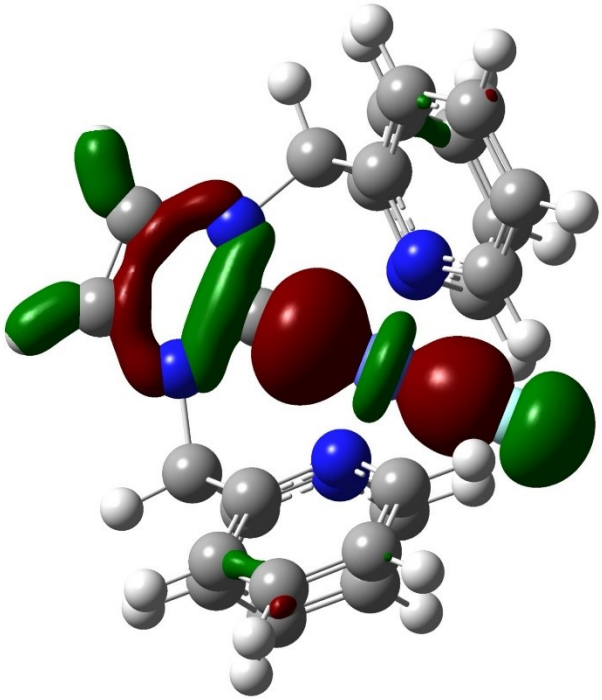
HOMO-17; significant π bonding Co (39.1%) and F (29.8%) with tiny bonding orbital between Co and C (1.51%)



HOMO-23; σ bonding between Co (4.90%) and F (4.39%) with carbene (0.276%)

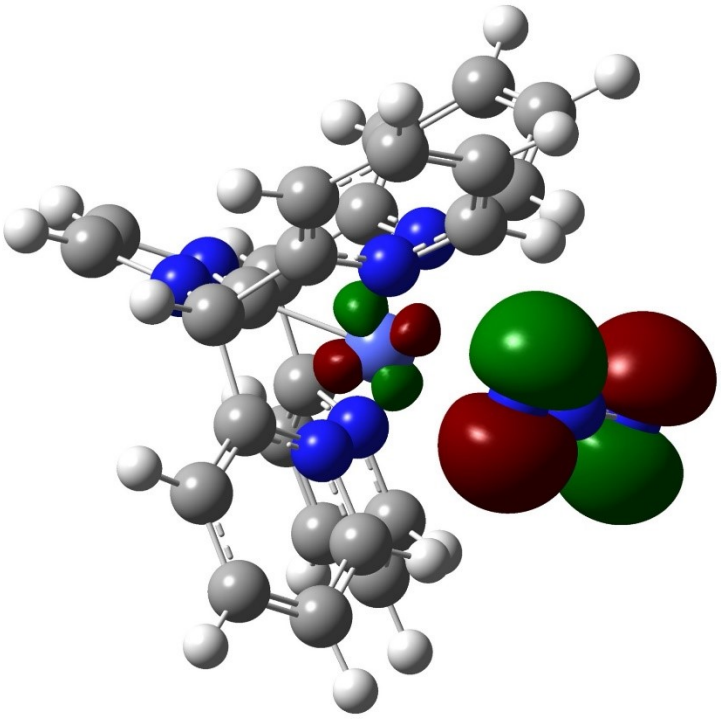


HOMO-24; strong σ bonding between Co (31.1%) and carbene (16.8%) with F (27.4%)

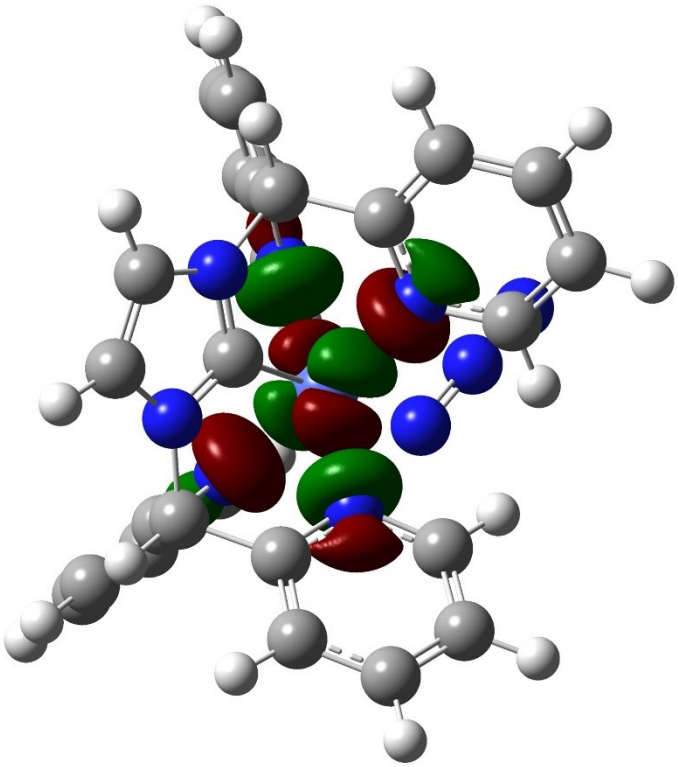


Azido complex Mayer bond order: C -0.836-Co-0.566-N(azide)

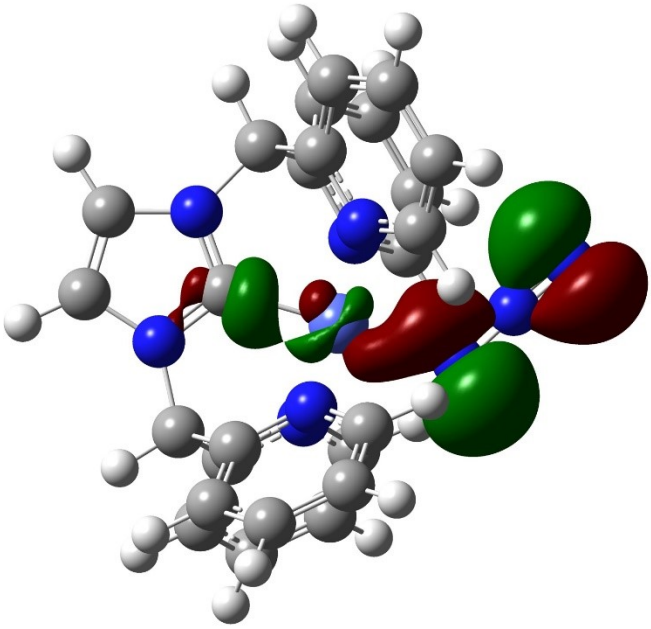
HOMO; Co (8.22%), N (azide donor) (45.7%), carbene (0.351%)



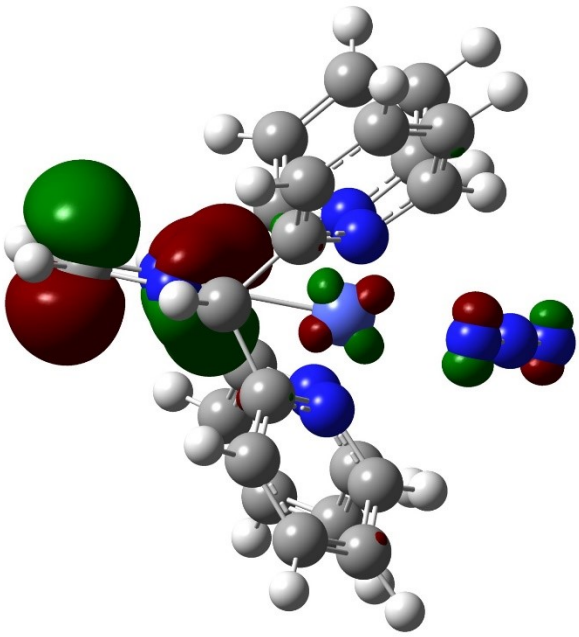
LUMO; Co (62.4%), N (azide donor) (0.00109%), carbene (0.00228%)



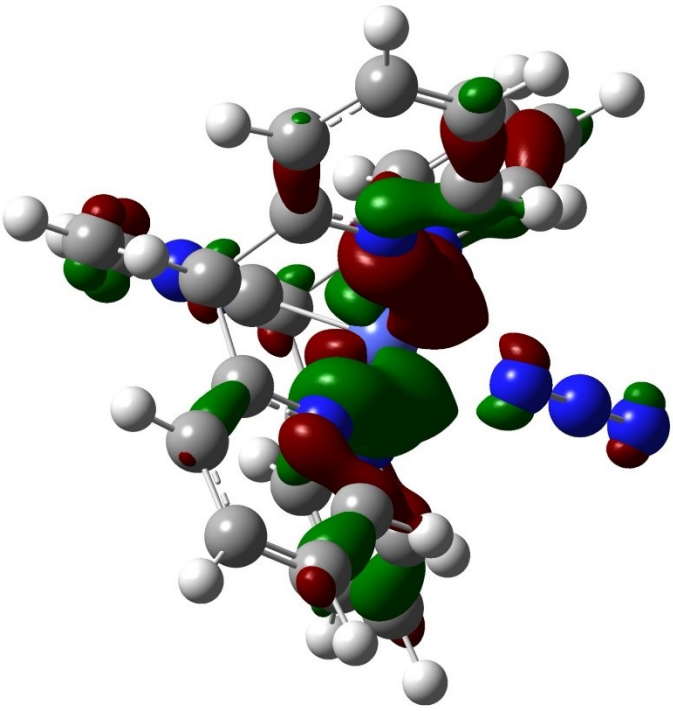
HOMO-1; Co (6.46%), N ((azide N) 49.0%), carbene (5.55%); Co-N σ bond.



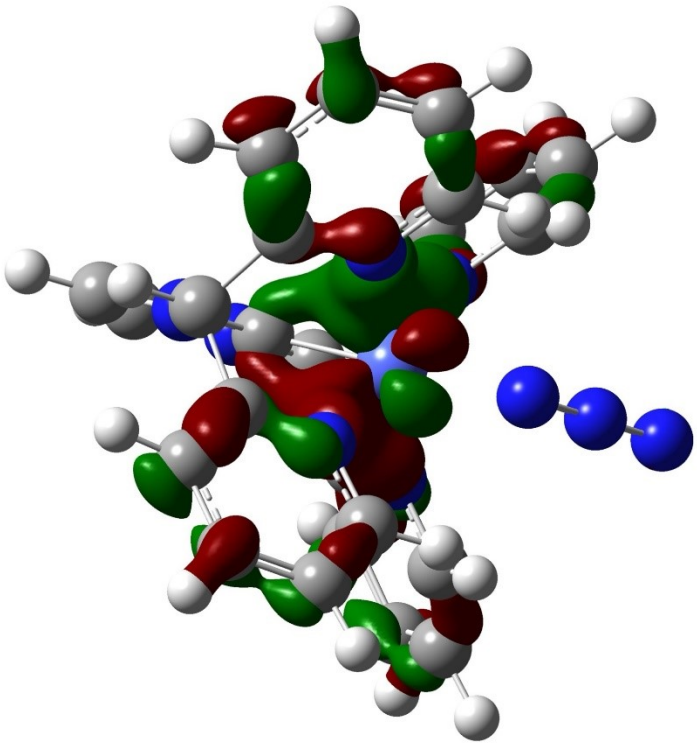
HOMO-2; Co (3.79%), N ((azide N) 2.34%), carbene (16.5%); very weak Co-N π bond.



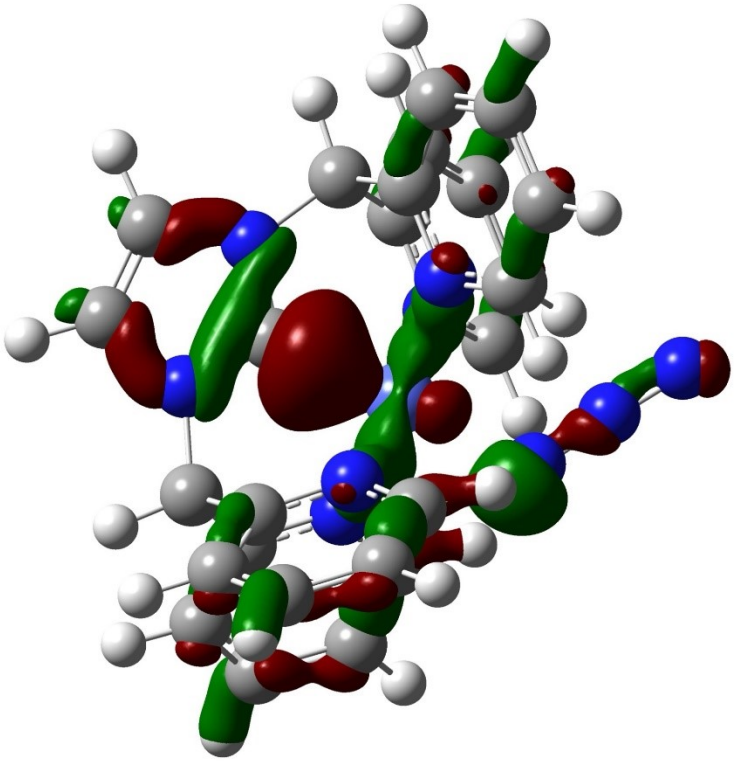
HOMO-12; Co (33.9%), N ((azide N) 1.91%), carbene (0.172%); weak Co-N π bond.



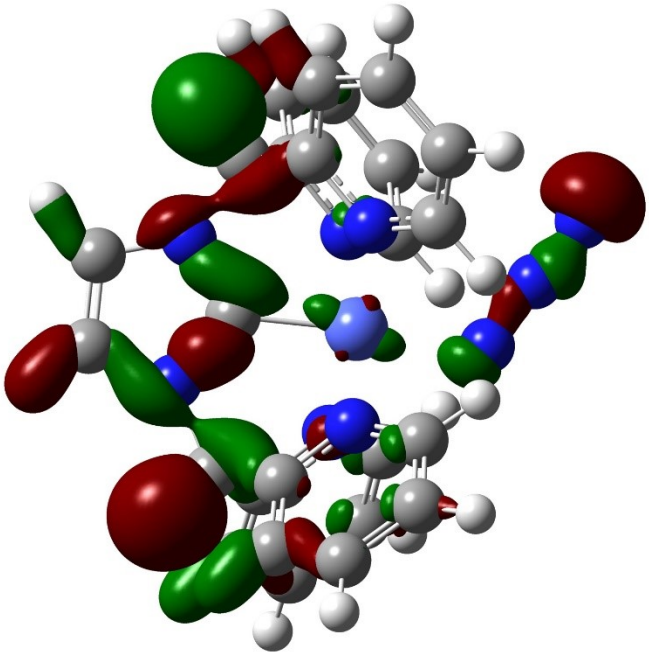
HOMO-16; Co (32.1%), N (azide N) 0.514%), carbene (2.75%); an extended π bond from the carbene C to the Co over the adjacent N donors from the ligand itself.



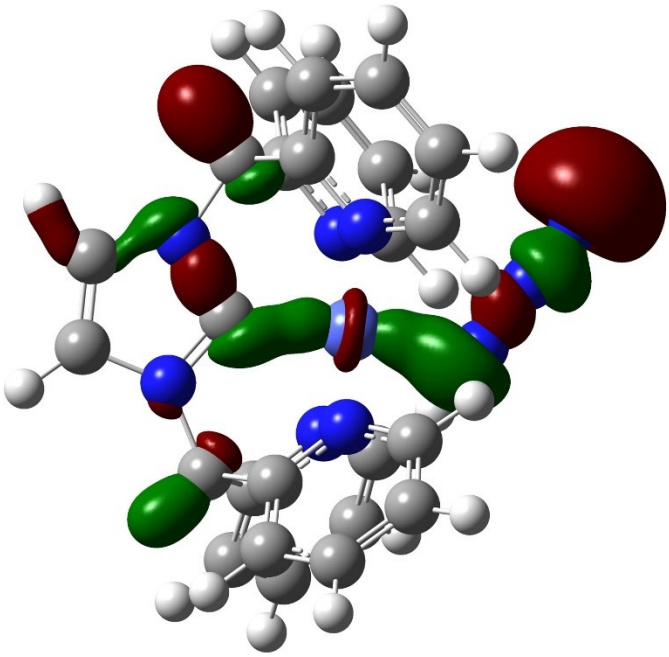
HOMO-18; Co (27.3%), N (azide donor) (6.06%) and carbene (19.9%); a strong Co-C σ bond.



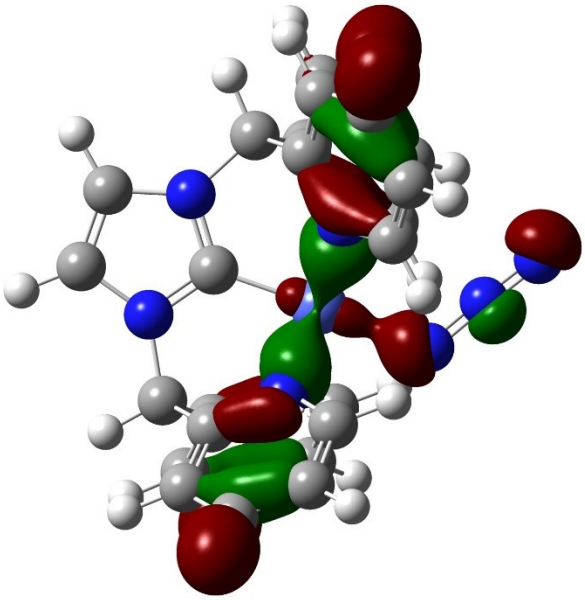
HOMO-24; Co (2.07%), N (azide donor) (1.88%) and carbene (4.78%); a weak N-Co-C σ bond.



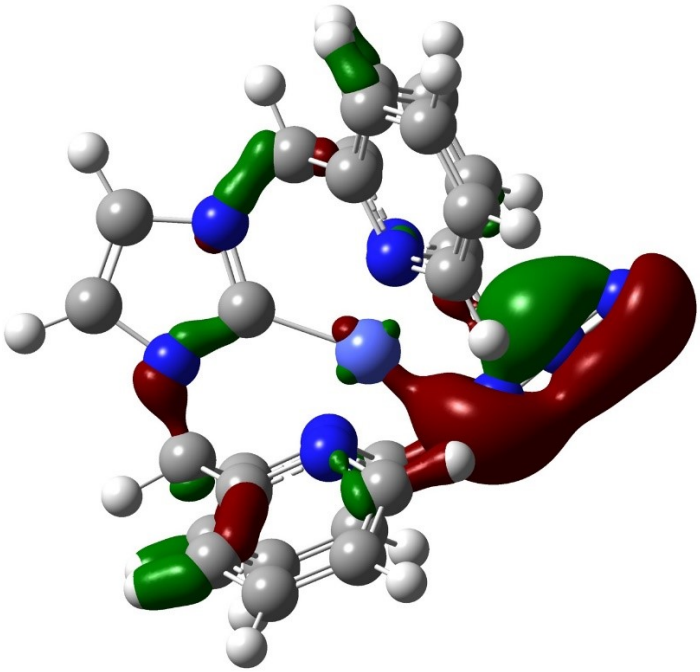
HOMO-25; Co (6.43%), N (azide donor) (9.29%) and carbene (3.12%); a banana σ bond over N-Co-C.



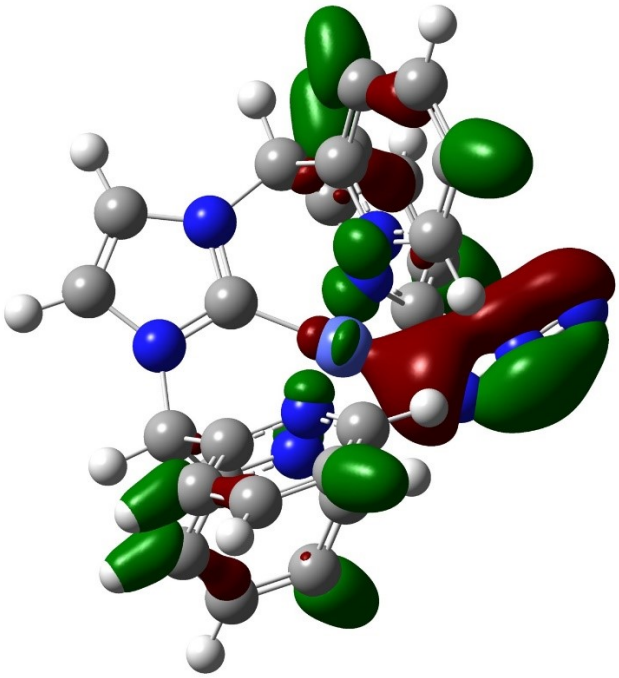
HOMO-37; Co (10.4%), N (azide donor) (3.01%) and carbene (0.761%); a weak N-Co σ bond.



HOMO-43; Co (3.54%), N (azide donor) (23.4%) and carbene (0.572%); a N-Co σ bond.



HOMO-46; Co (5.23%), N (azide donor) (15.7%) and carbene (0.361%); a N-Co σ bond.



HOMO-49; Co (7.91%), N (azide donor) (16.3%) and carbene (1.25%); a N-Co-C σ bond.

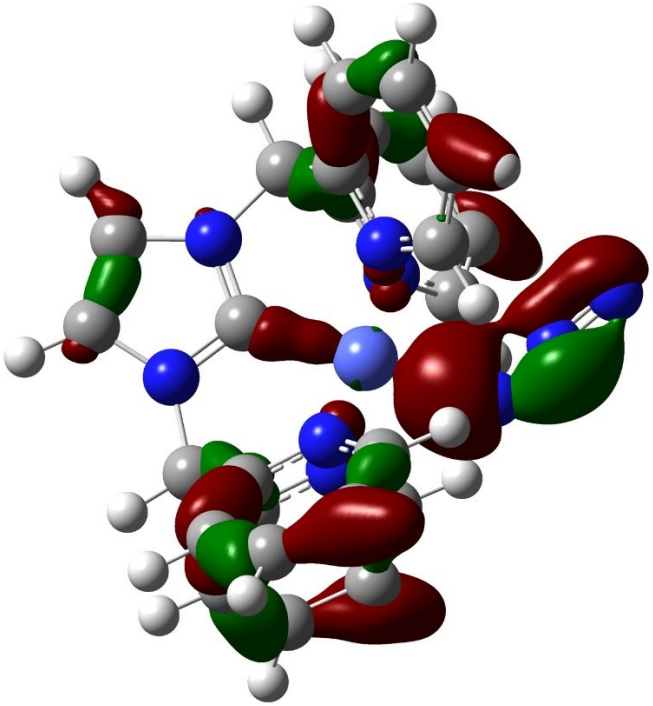
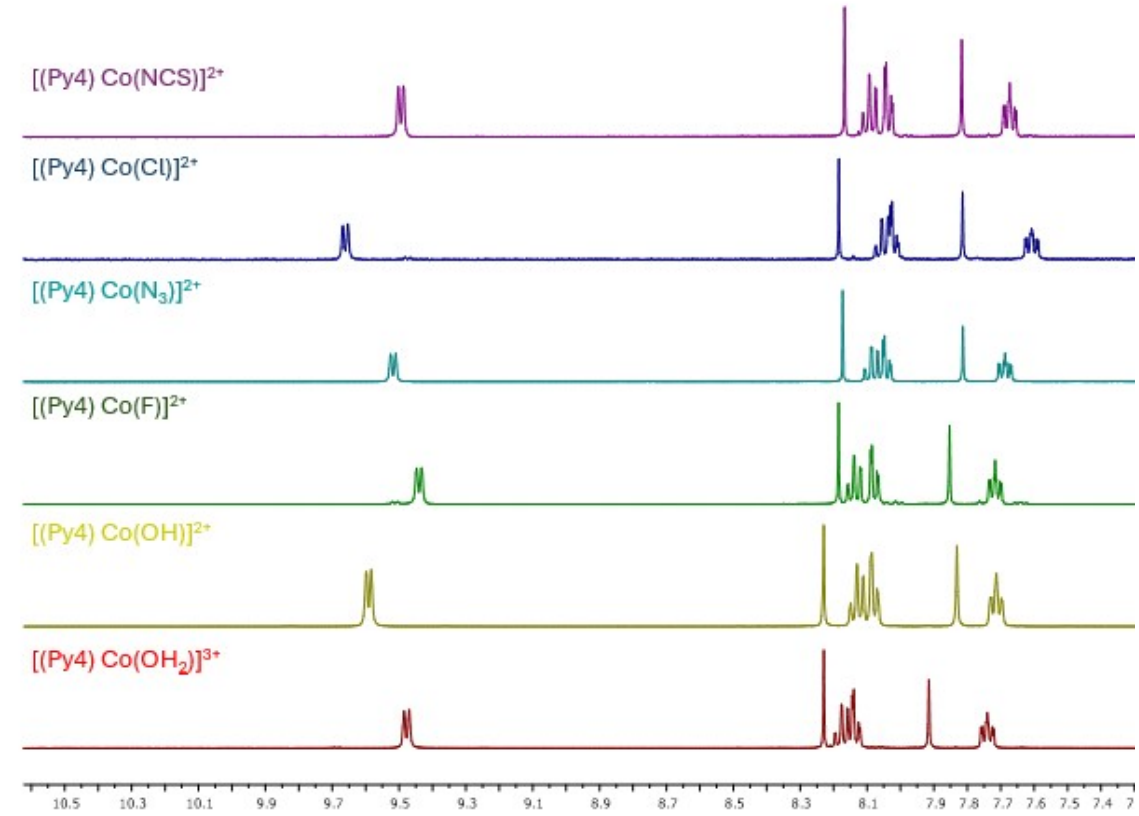


**Figure S6**: $^{1}H$ and $^{13}C$ spectra of $[Co(PY4Im)(X)]^{2+}$ complexes in $D_2O$



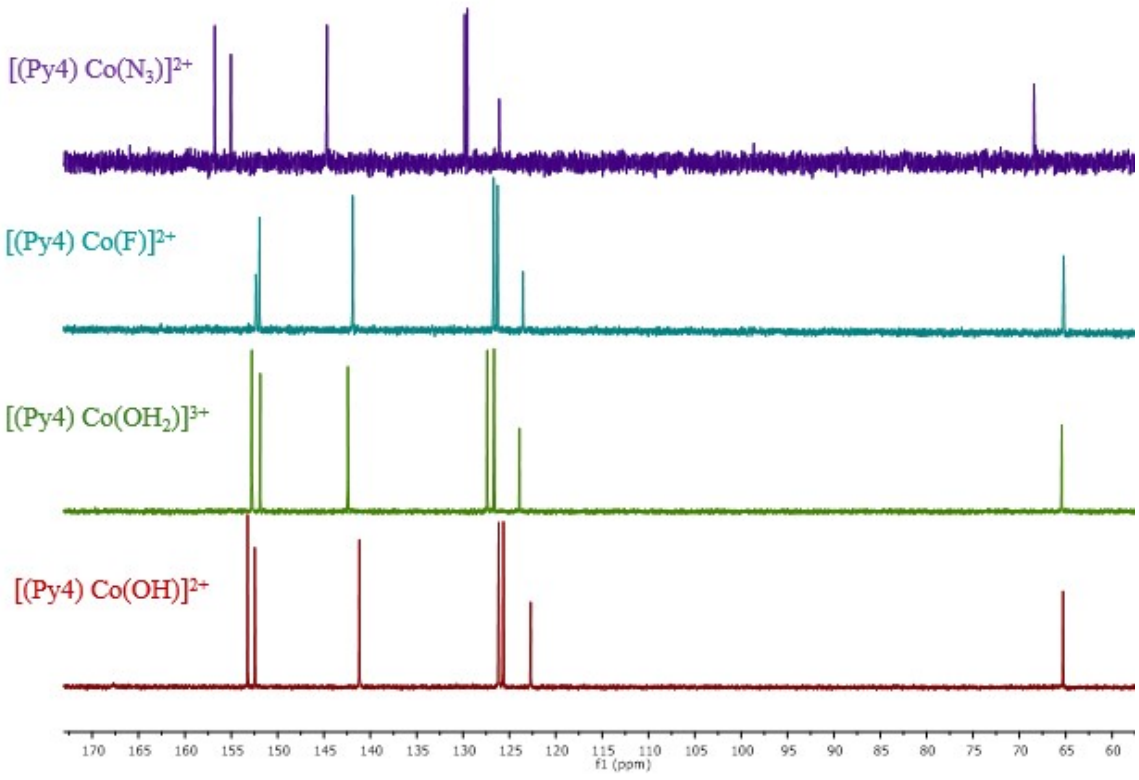
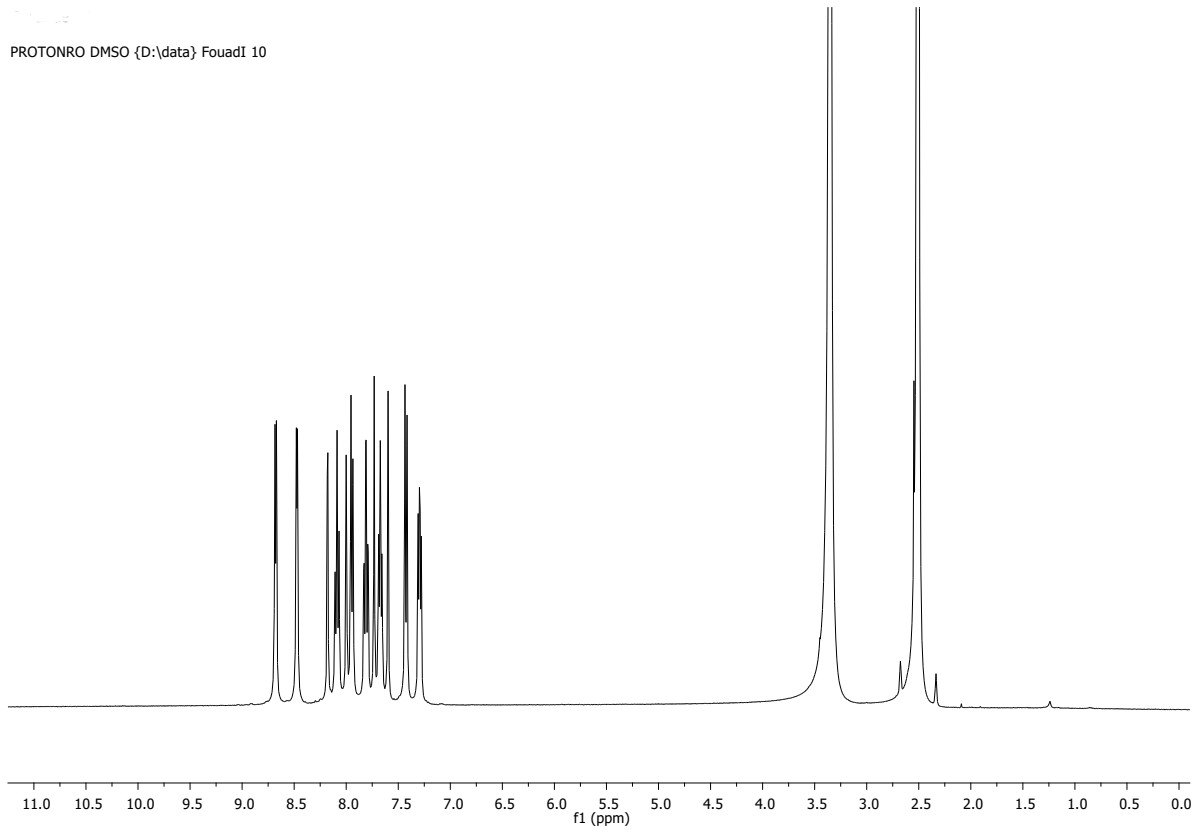



**Figure S7**: $^{1}H$ and $^{13}C$ spectra of $[Co(PY4Im)(N_3)_3]$ in $d^6$-DMSO



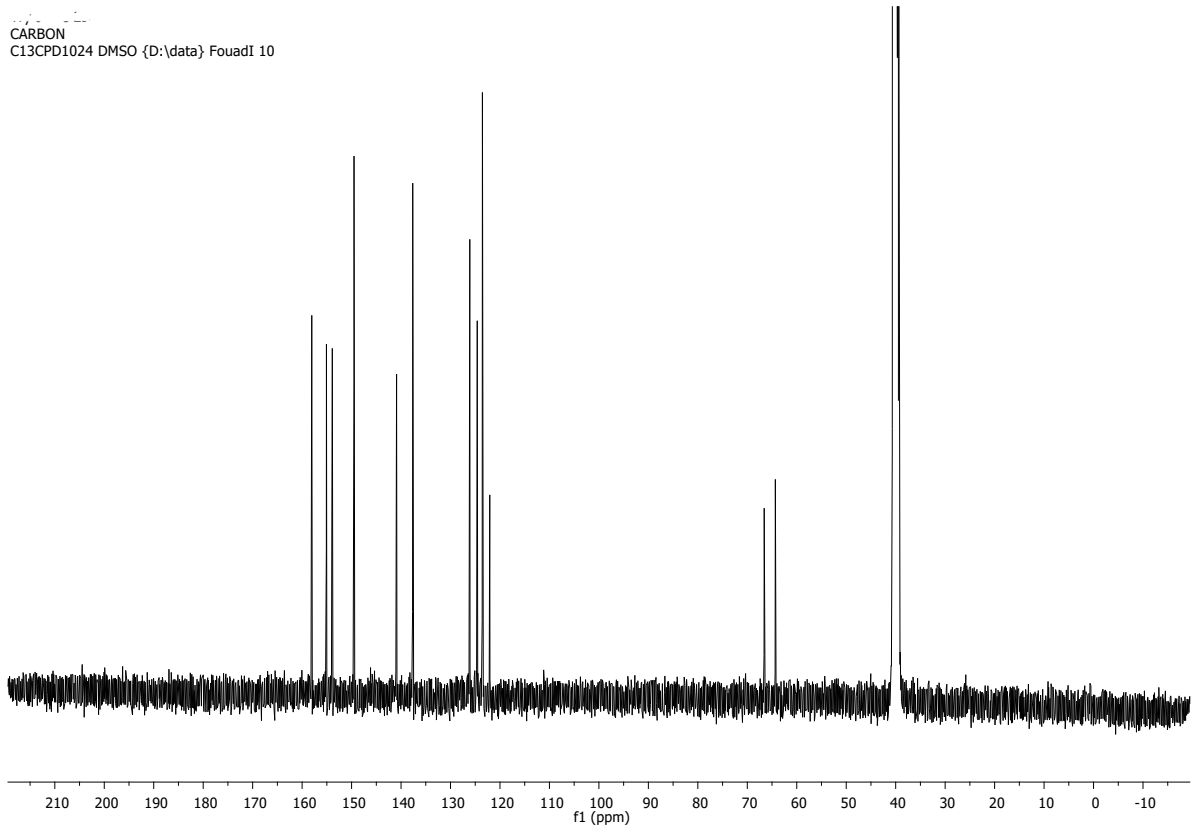
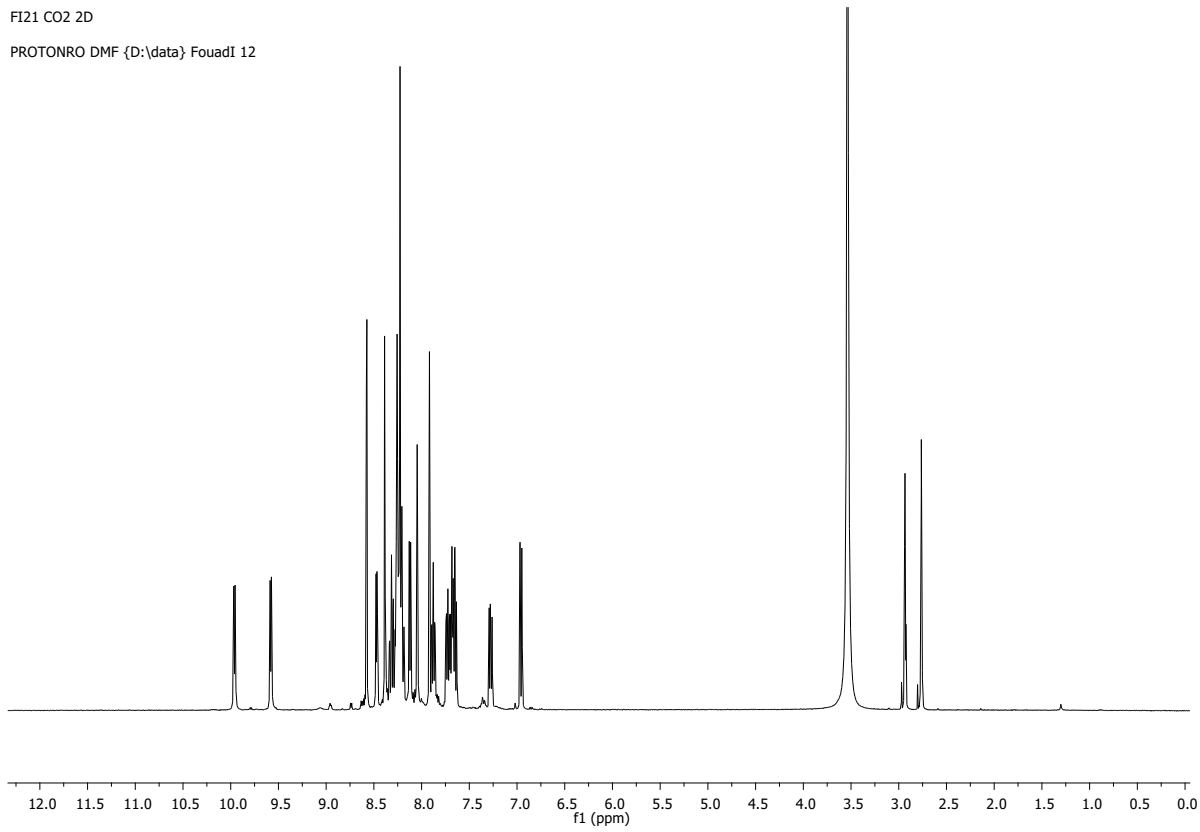



**Figure S8**: $^{1}H$ and $^{13}C$ spectra of $[Co(PY4Im)(O_2CO)]^{+}$ in $d^7$-DMF



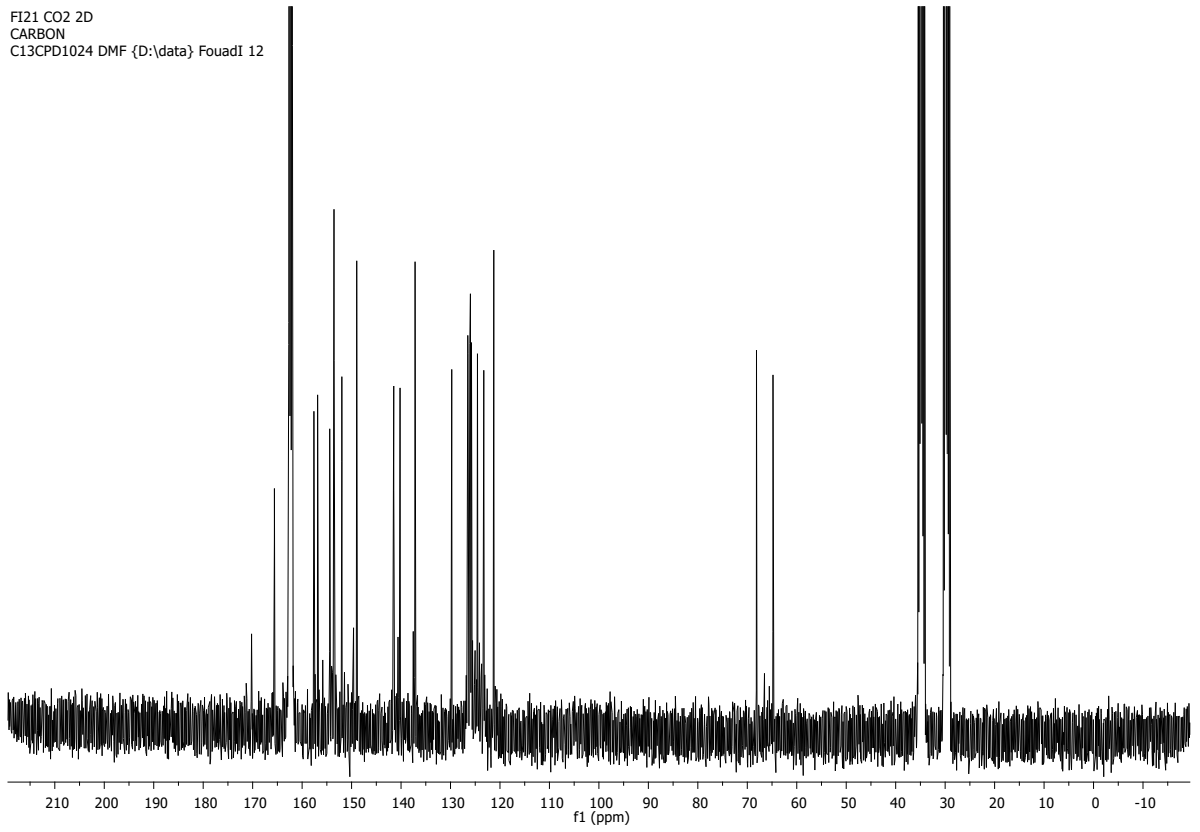



**Figure S9**: Residual density plot for $[(PY4Im)Co(NCS)](ClO_4)_{1.5}(NCS)_{0.5}.2H_2O$

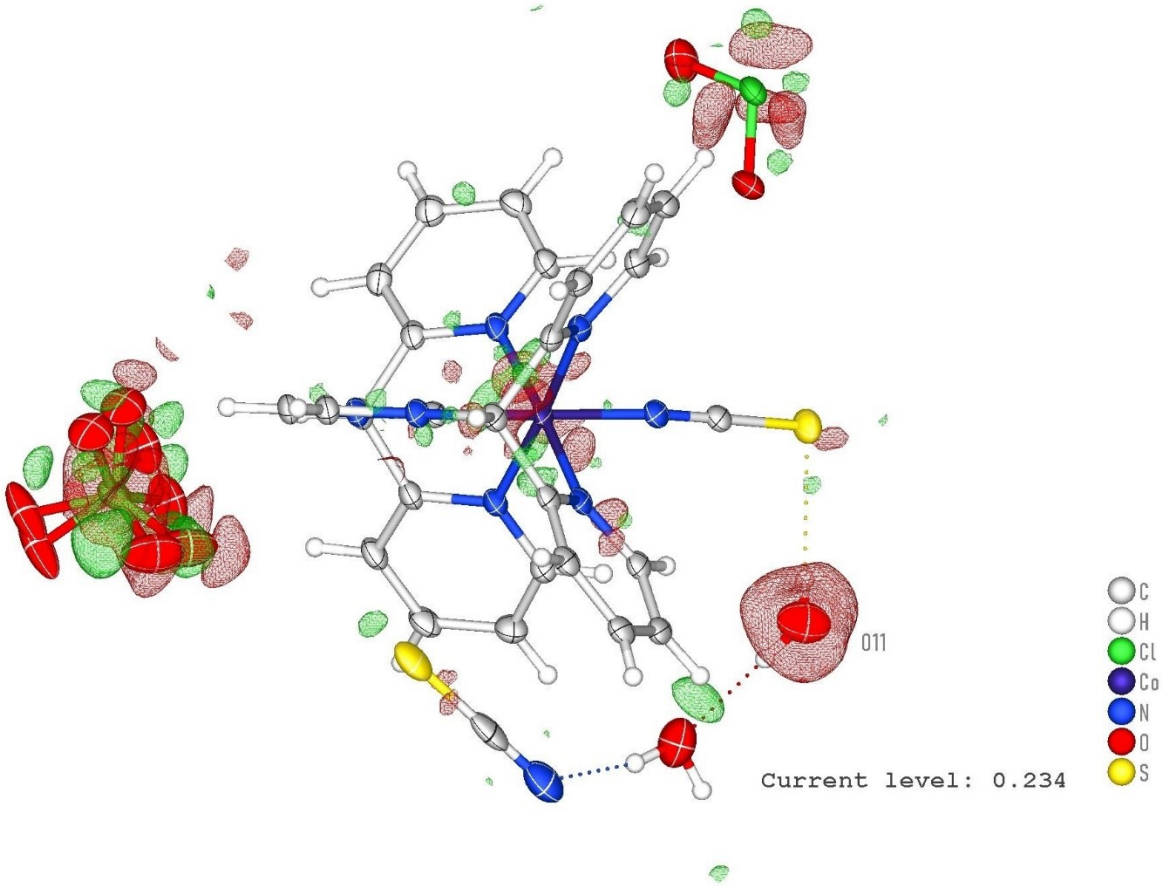



**Figure S10**: Residual density plot for $[(PY4Im)Co(ONO)](ClO_4)_2.1.5H_2O$

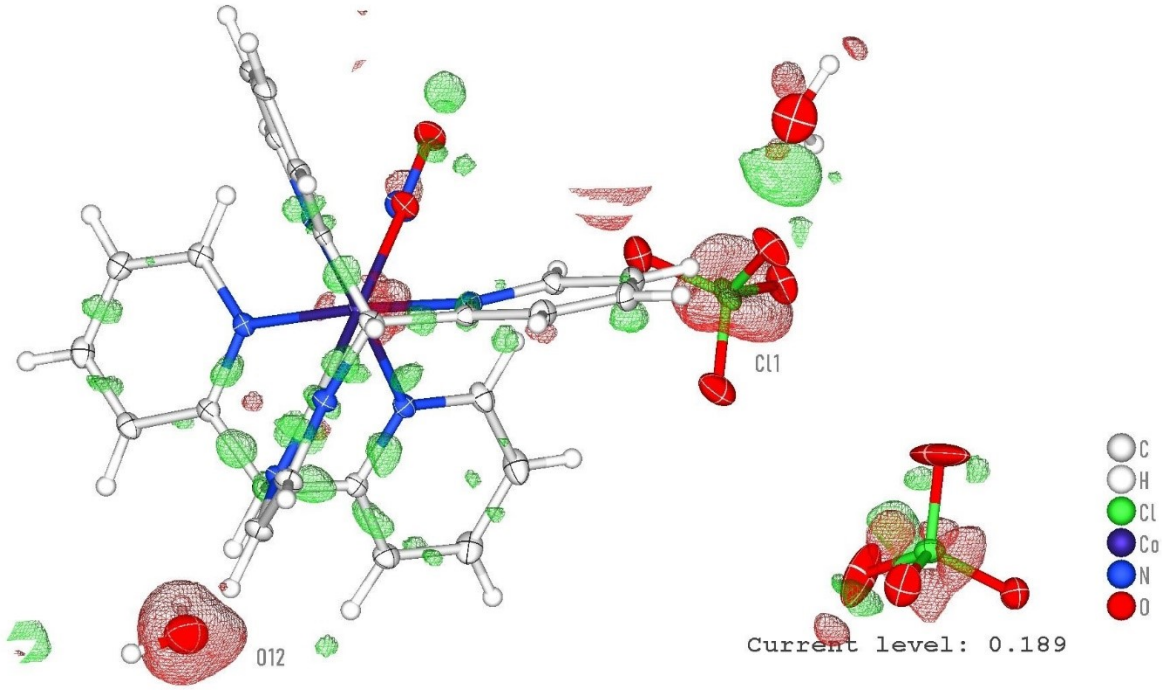


**Figure S11**: Residual density plot for *fac*-[(PY4Im-κ$^3$*N,N',C*)Co($N_3$)$_3$].($CH_3$)$_2$SO