SUPPORTING INFORMATION

In Search of Redox Noninnocence between a Tetrazine Pincer Ligand and Monovalent Copper

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MSC#12122 Single Crystal X-ray structure determination of Cu(btzp)$_2$PF$_6$ Hui

A dark red crystal (approximate dimensions 0.28 x 0.07 x 0.05 mm^3) was placed onto the tip of a glass capillary and mounted on an Apex Kappa Duo diffractometer and measured at 150(2) K.

A preliminary set of cell constants was calculated from reflections harvested from three sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 90 seconds and a detector distance of 5.0 cm. A randomly oriented region of reciprocal space was surveyed to achieve complete data with a redundancy of 4. Sections of frames were collected with 0.50º steps in ω and ϕ. Data to a resolution of 0.84 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 6125 strong reflections from the actual data collection after integration (SAINT).[1] The intensity data were corrected for absorption (SADABS).[2] The space group $P2_1/n$ was determined based on intensity statistics and systematic absences. The structure was solved using SHELXS-97[3] and refined with SHELXL-97.[3] A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with individual relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0433 and wR2 = 0.1110 (F^2, all data). The remaining electron density is located along the bonds.

Two solvent molecules, acetonitrile, were found to be present in the crystal lattice, however they are all outside interaction range of copper, as judged by van der Waals radii sums. Hexafluorophosphate, the non-coordinating counterion was found to be disordered (79:21). The unit cell shows no unusual contacts

to PF_6^- (shortest Cu/P distance is 6.27 Å), and there is one contact of 3.06 Å from a guest MeCN nitrogen to a tetrazine ring carbon (C2).

[1] SAINT, Bruker Analytical X-Ray Systems, Madison, WI, current version.
[2] An empirical correction for absorption anisotropy, R. Blessing, Acta Cryst. A51, 33 - 38 (1995).
[3] SHELXTL-Plus, Bruker Analytical X-Ray Systems, Madison, WI, current version.

Electronic spectrum.

Solid $Cu(btzp)_2[PF_6]$ is almost black, and with 5mg of this in ~0.5 mL of CD_3CN, the solution color is black/red. With 1:10 dilution, this solution becomes increasingly red. In addition to showing the three peaks seen in btzp itself (Figure S3), hence assigned as ligand localized, the complex (Figure S1 and S2) has an additional very weak peak in the 400-450 region.
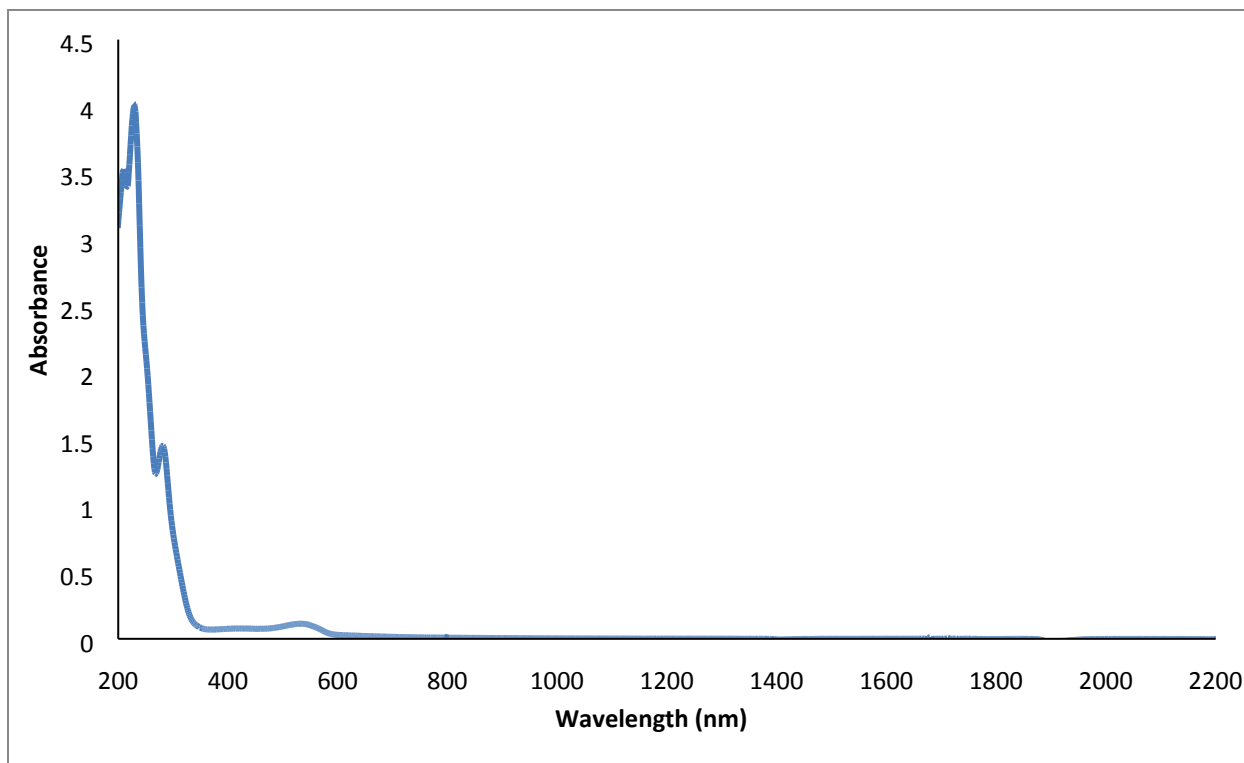

Figure S1. UV-Vis spectrum of 1mM Cu(btzp)$_2$PF$_6$ in acetonitrile from 200 to 2200 nm.

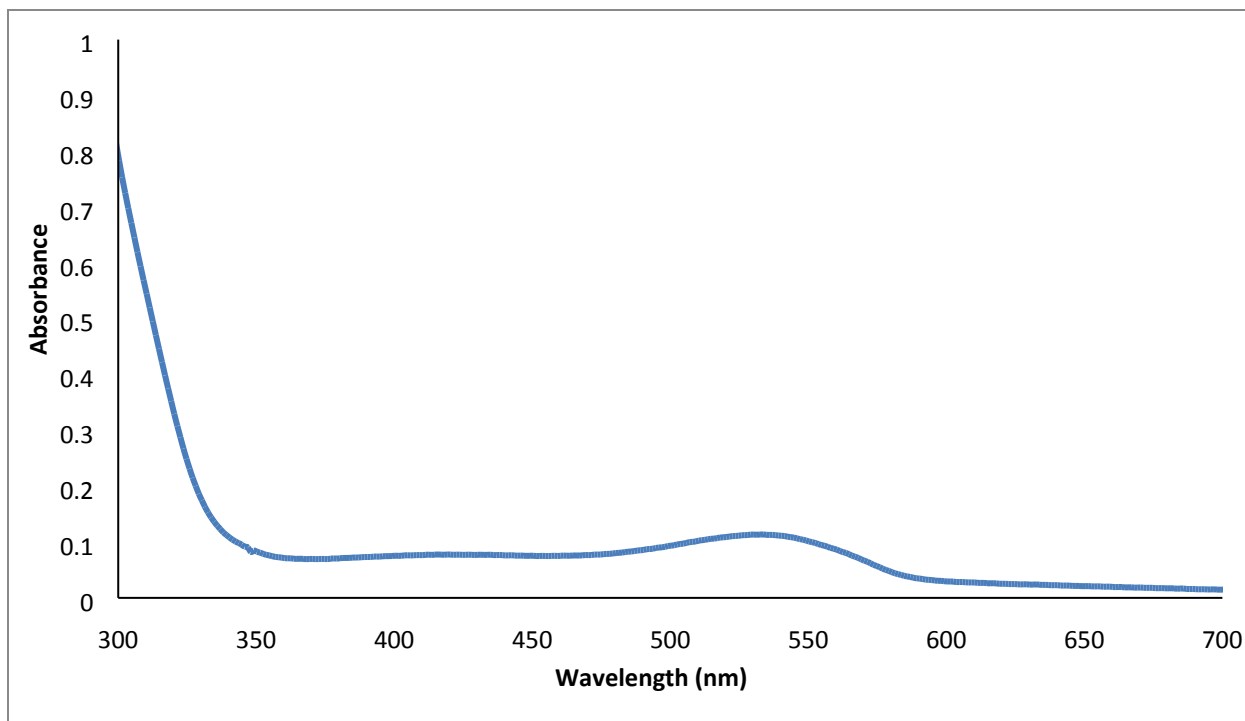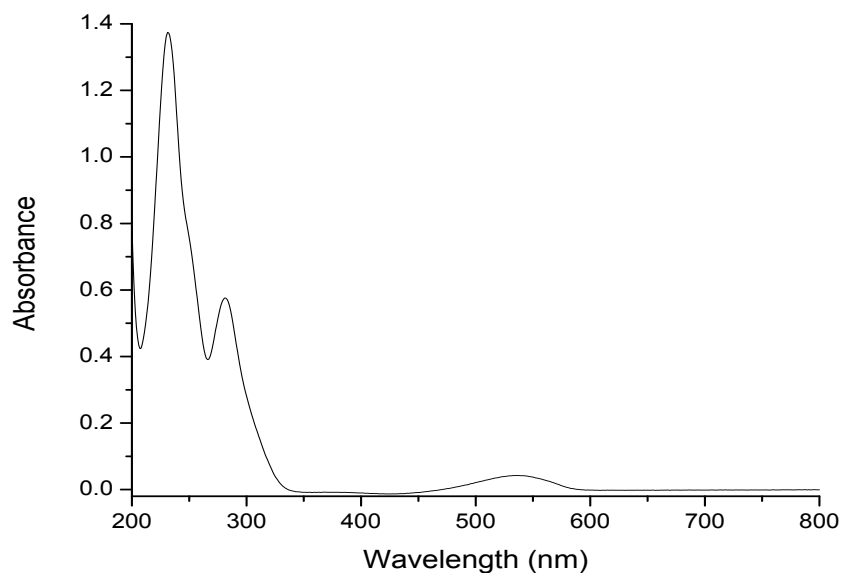**Figure S2. UV-Vis spectrum of 1mM CuL$_2$PF$_6$ in acetonitrile from 300 to 700 nm.**

Figure S3. UV-Vis spectrum of 0.05 mM btzp in acetonitrile from 200 to 800 nm.

Reactivity

There has been a good deal of productive activity recently is using pendant Bronsted basicity to promote heterolytic splitting of H$_2$: the Bronsted base accepts H$^+$ and the metal accepts H$^-$. We therefore probed

whether such reactivity could exist for $Cu(btzp)_2^+$. Exposure of this cation, dissolved in MeCN, to 1 atm of H_2 showed no color change nor any change in the ^1H NMR spectrum over a period of 24 h at 25 °C, indicating that the envisioned heterolysis does not occur. There was not even any reduction to bulk copper metal.

Electronic structure calculations were carried out using DFT[1] as implemented in Gaussian09.[2] Geometry optimizations were performed at the B3LYP/LANL2DZ/6-31G(d,p)[3-7] level of theory with no symmetry constraints. All optimized structures were confirmed to have stable wavefunctions,[8-9] and to be local minima by analyzing the harmonic frequencies.[10-11] Cartesian coordinates and frequencies for all optimized species may be found in Tables S1 and S2, respectively. We begin calculations assuming the wavefunction is unrestricted. Calculations that began with an unpaired electron on Cu and another of opposite spin on the ligand(s) collapsed back to a restricted wavefunction. Wavefunction stability analysis also suggested that, for the geometries we tested, the restricted wavefunction is stable with respect to a breaking of the alpha and beta spin densities.

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Table S1. Cartesian Coordinates (in Å) for Optimized Structures.

[Cu(btzp)₂]⁺ *S*=0

```
Cu    -0.005052     0.511502    -0.023446
 N     0.790088    -0.227229    -1.921829
 C     0.255584    -1.172343    -2.710081
 C     1.953134     0.335237    -2.288823
 C     0.866451    -1.589992    -3.900103
 C     2.632763    -0.020702    -3.458822
 C     2.072233    -1.001506    -4.273548
 H     0.392122    -2.355679    -4.501483
 H     3.567730     0.467719    -3.705011
 H     2.568697    -1.303499    -5.189827
 C     2.481748     1.374634    -1.376959
 C     3.370464     3.208092     0.211394
 C    -1.031120    -1.767010    -2.268536
 C    -3.287383    -2.781467    -1.536450
 N     1.763331     1.671975    -0.281234
 N     2.212208     2.609912     0.535861
 N     4.105114     2.895571    -0.882512
 N     3.648302     1.965112    -1.687158
 N    -1.555358    -1.359064    -1.106404
 N    -2.713429    -1.871630    -0.729421
 N    -2.738766    -3.214688    -2.695492
 N    -1.594355    -2.694531    -3.067731
 C    -4.606529    -3.360439    -1.138456
 H    -4.894657    -3.002655    -0.149834
 H    -5.375177    -3.076459    -1.864847
 H    -4.554066    -4.452976    -1.138618
 C     3.889886     4.285639     1.107166
 H     3.890074     5.243812     0.576905
 H     3.269585     4.368557     1.999711
 H     4.925348     4.074725     1.388878
 N    -0.784543    -0.067203     1.936870
 C    -1.949670     0.517151     2.260684
 C    -0.238822    -0.936494     2.801135
 C    -2.619699     0.260441     3.461729
 C    -0.839913    -1.252820     4.026912
 C    -2.047503    -0.641767     4.355312
 H    -3.556639     0.762364     3.670309
 H    -0.356663    -1.960039     4.689625
 H    -2.536499    -0.865765     5.297627
 C     1.049395    -1.559525     2.405455
 N     1.567237    -1.248227     1.211057
 N     2.725110    -1.787449     0.872483
 C     3.305498    -2.625444     1.749588
 C    -2.492066     1.467942     1.264125
 N    -1.783249     1.672183     0.141186
 N    -2.244796     2.531200    -0.752262
 C    -3.405617     3.147140    -0.473650
 N    -4.130487     2.927505     0.649079
 N    -3.661131     2.075189     1.529397
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```
N     1.620769    -2.413370     3.277792
N     2.765080    -2.959465     2.944840
C     4.623087    -3.234521     1.393655
H     5.391956    -2.904488     2.099901
H     4.566758    -4.324441     1.468255
H     4.912910    -2.946934     0.382867
C    -3.940516     4.136101    -1.458096
H    -3.311533     4.163528    -2.347974
H    -4.966315     3.875300    -1.734111
H    -3.973429     5.132748    -1.005875
```

[Cu(btzp)₂]⁺ _S_=1

```
Cu   -0.000210    -0.002729    -0.182409
N    -0.001542    -0.018285    -2.168494
C     0.182810    -1.184474    -2.814194
C    -0.187479     1.138011    -2.831187
C     0.187505    -1.233225    -4.208166
C    -0.195127     1.165889    -4.225802
C    -0.004522    -0.038844    -4.911574
H     0.337721    -2.181955    -4.710144
H    -0.346513     2.107073    -4.741437
H    -0.005645    -0.047055    -5.996368
C    -0.367983     2.279875    -1.935527
C    -0.674194     4.214589    -0.248285
C     0.364645    -2.312666    -1.901723
C     0.672830    -4.222160    -0.186414
N    -0.318034     1.996770    -0.604879
N    -0.477850     3.002516     0.265775
N    -0.724661     4.503125    -1.583331
N    -0.566003     3.499384    -2.429062
N     0.317019    -2.009808    -0.575531
N     0.477785    -3.002323     0.309552
N     0.721210    -4.530465    -1.517177
N     0.561564    -3.539767    -2.377421
C     0.856122    -5.359032     0.767987
H     0.796453    -5.007805     1.798355
H     0.090076    -6.120963     0.593325
H     1.825476    -5.837879     0.597582
C    -0.856510     5.365525     0.689356
H    -1.827163     5.840179     0.514613
H    -0.793292     5.030083     1.724766
H    -0.092289     6.125969     0.500842
N     0.002227     0.014144     1.928534
C    -1.144634    -0.140724     2.616204
C     1.149946     0.180630     2.611985
C    -1.185178    -0.134584     4.014667
C     1.192348     0.197581     4.010330
C     0.004069     0.037283     4.716817
H    -2.136159    -0.263674     4.516359
H     2.144008     0.334933     4.508526
H     0.004797     0.046180     5.801775
C     2.394219     0.350442     1.822460
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N      2.300719     0.339931     0.490037
N      3.399183     0.489683    -0.225868
C      4.555084     0.646722     0.443436
C     -2.390015    -0.322489     1.831168
N     -2.297808    -0.337165     0.498762
N     -3.397773    -0.494426    -0.213378
C     -4.553802    -0.632547     0.459740
N     -4.645531    -0.624202     1.812317
N     -3.546130    -0.465860     2.506957
N      3.551043     0.505485     2.494308
N      4.649122     0.656205     1.795767
C      5.815198     0.825140    -0.337629
H      6.243537     1.812328    -0.135032
H      6.557606     0.084040    -0.027208
H      5.616787     0.728001    -1.404972
C     -5.817286    -0.807002    -0.316763
H     -5.604382    -0.838569    -1.385246
H     -6.321203    -1.728883    -0.011070
H     -6.503781     0.018910    -0.104212
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Table S2. Frequencies (in cm⁻¹) for Optimized Structures.

[Cu(btzp)₂]⁺ *S*=0

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   9.7776     12.6871     13.7933
  23.8243     24.0989     33.0893
  37.6872     39.5819     42.5769
  44.3351     46.2441     51.0939
  53.5812     55.3059     58.0909
  63.6922     67.6537     76.9314
 104.8305    105.4081    108.5190
 117.7926    155.8359    159.7597
 161.2555    164.1570    170.1808
 186.8874    203.1123    257.8860
 264.9846    322.7447    322.9590
 330.2466    330.3778    332.6312
 336.1191    345.7590    346.0653
 357.7656    357.9560    363.3884
 368.6917    370.0150    375.6387
 446.3320    447.3204    454.2999
 458.2784    464.8146    470.6208
 539.7633    541.2536    542.2704
 543.4921    625.9592    626.1606
 630.2989    632.1207    677.6515
 677.9104    684.0636    684.4951
 684.9660    685.6472    699.9920
 700.1039    763.0977    763.9530
 811.6930    811.9128    813.9604
 813.9760    834.7677    836.1348
 865.3456    865.6251    868.4859
 870.0110    885.0505    885.5030
 976.8914    977.6182    983.5236
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 984.1100    989.6766    990.3871
1024.6366   1026.1790   1036.8338
1037.0403   1059.2913   1059.4964
1060.1266   1060.2314   1060.3738
1060.5572   1065.6027   1066.0993
1080.8395   1080.9604   1104.1593
1104.3011   1115.4888   1116.6326
1140.0844   1140.7477   1164.4956
1165.0340   1195.8157   1197.3798
1299.8576   1300.4038   1324.9769
1325.2434   1329.4868   1329.5588
1332.3612   1333.7687   1364.3347
1364.7272   1397.6426   1398.0410
1409.1893   1409.5078   1436.2558
1436.3447   1439.3200   1439.4492
1459.5770   1460.5577   1473.3324
1473.8606   1482.3014   1482.3656
1482.7290   1482.9875   1492.0975
1492.4225   1501.2410   1501.8064
1511.5396   1513.0482   1518.6847
1519.0999   1542.0910   1542.8588
1548.3624   1549.8905   1629.1073
1629.3152   1638.5631   1638.8618
3066.6014   3066.7541   3066.9874
3067.1287   3129.6102   3129.8190
3130.3219   3130.6759   3176.9972
3177.0481   3178.2851   3178.6805
3219.2773   3219.4630   3245.8238
3246.1942   3248.2429   3248.4076
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[Cu(btzp)$_2$]$^+$ *S*=1

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   6.8035     13.7833     16.3241
  21.5758     33.2996     33.4207
  36.7146     44.0440     54.1718
  61.1346     63.9488     79.1806
  80.4371     84.2390     85.3106
  88.2740     94.6730     97.3952
 102.7720    135.4706    158.0567
 159.1948    169.3575    179.1248
 182.7502    192.0939    198.6109
 234.4187    244.4021    266.4980
 290.5676    316.4640    322.6071
 328.5672    333.2201    338.1146
 348.3906    350.0167    353.0445
 366.3154    367.2983    368.5944
 369.7216    373.0886    379.0998
 450.0558    455.7078    455.8467
 466.0911    473.0972    497.8737
 534.3453    542.8742    557.1521
 569.7021    617.5958    626.2136
 634.2170    640.3432    667.3340
 677.5850    679.6695    682.2281
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 683.0560    683.5918    703.6398
 707.7344    745.7138    770.1507
 777.3590    786.6469    811.1568
 811.5547    817.1148    836.1574
 846.7929    864.1342    866.5690
 869.6656    870.4385    884.9230
 965.1667    982.5993    985.1978
 988.9900    990.8075    992.4775
1021.6939   1030.2974   1036.5743
1043.7182   1058.6256   1058.8036
1059.0731   1059.3048   1059.5165
1065.1206   1065.5658   1079.7278
1081.4731   1081.5867   1092.6146
1095.4430   1104.3572   1122.0786
1137.5512   1143.4391   1145.1647
1168.6280   1178.0620   1202.2598
1235.7767   1257.7346   1291.4839
1300.2667   1303.4115   1319.8789
1326.0487   1327.8356   1338.5891
1352.5769   1358.0020   1366.9518
1396.4994   1407.3228   1408.6011
1413.9050   1435.3748   1436.0376
1438.3724   1438.8984   1448.5663
1463.1019   1465.1376   1473.1908
1480.9657   1481.0788   1481.5537
1481.5761   1493.7621   1496.8488
1497.2196   1504.2605   1521.9198
1523.4559   1523.6632   1549.6911
1551.7230   1553.4100   1590.1116
1630.5150   1640.9897   1643.2650
3065.6083   3065.6481   3066.8981
3067.1590   3127.1710   3127.1945
3129.7377   3129.8986   3174.4308
3174.5435   3180.0678   3180.1247
3220.4716   3221.8735   3240.0190
3242.7713   3248.6711   3250.3522
```