SUPPORTING INFORMATION

Chemical Implications of Incompatible Ligand vs. Metal Coordination Geometry Preferences

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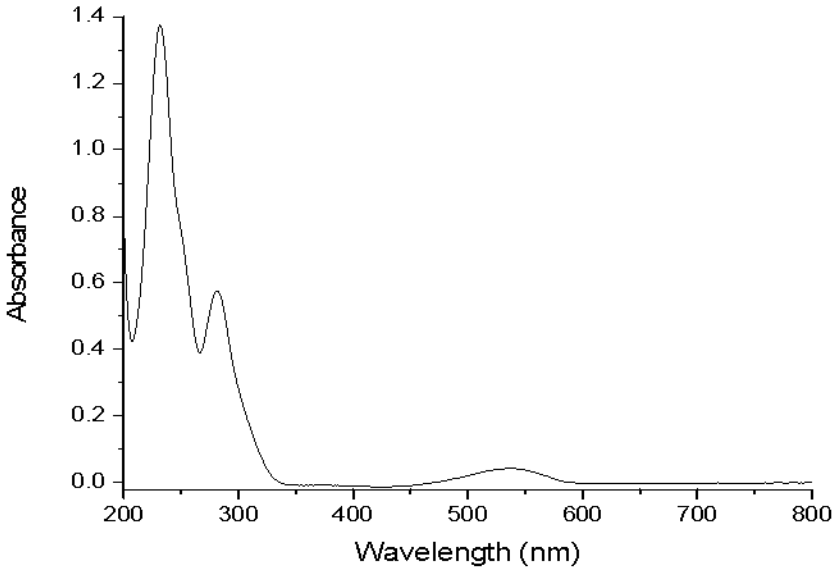

Figure S1. UV-Vis spectrum (200 – 800 nm) of 0.05mM (btzp)CuCl in acetonitrile.

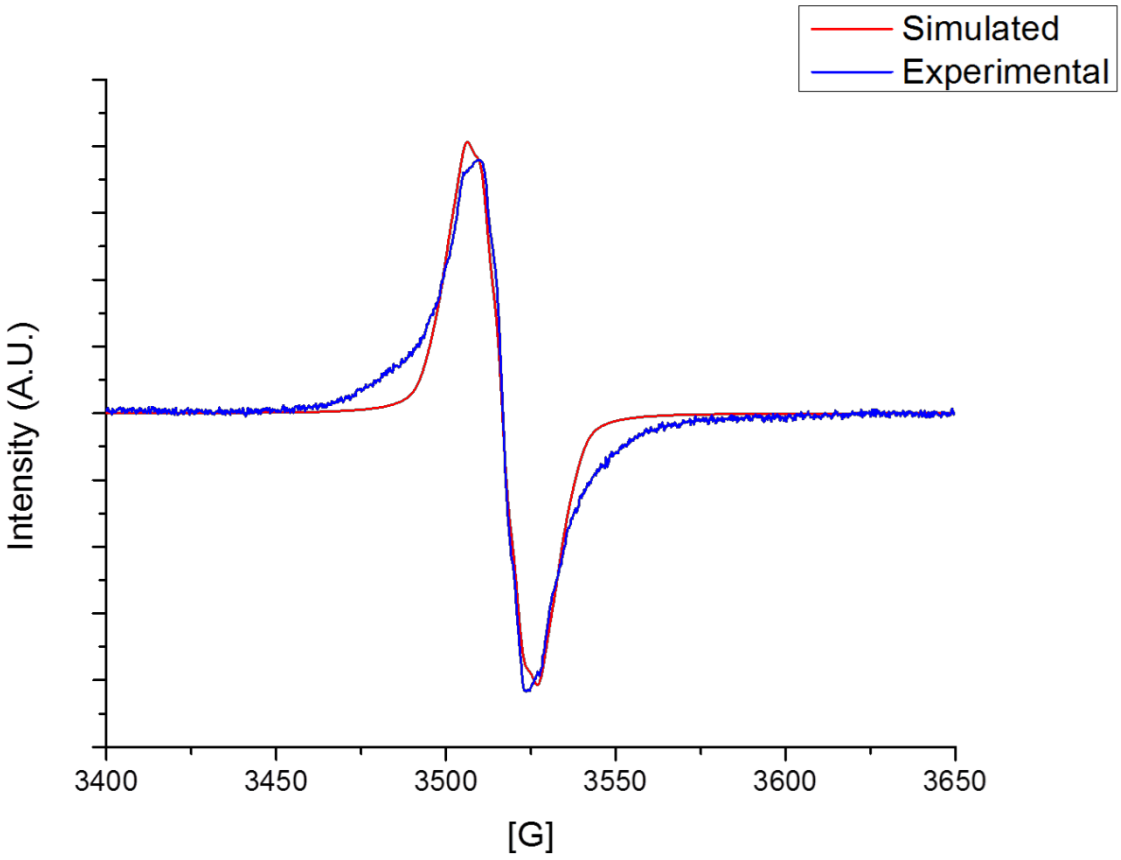

Figure S2. Experimental and simulated (g = 2.0042; A_N = 4.6 G) X-band EPR spectrum of solid (btzp)Cu suspended in MeCN.

Single crystal x-ray diffraction structure determination of (btzp)CuCl MSC#12074

A red crystal (approximate dimensions 0.32 x 0.1 x 0.075 mm^3) was placed onto the tip of a MiTiGen Pen (0.3 mm) and mounted on an Apex Kappa Duo diffractometer and measured at 260(2) K.

Data collection

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 80 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 0.846 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 1283 strong reflections from the actual data collection after integration (SAINT).[1] The intensity data were corrected for absorption (SADABS).[2]

Structure solution and refinement

The space group P2(1)/m was determined based on intensity statistics and systematic absences. The structure was solved using SHELXS-97[3] and refined with SHELXL-97.[4] 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 = 0.0535 and wR2 = 0.1305 (F^2, all data). The remaining electron density is located along bonds.

Structure description

The structure exists as a polymer in the solid state. The asymmetric unit only contains half of the molecular structure since the complex lies on a special position: the compound lies on a mirror plane that bisects the Cu1, N5, Cu6, Cl1 atoms. The crystallographic a axis length is short, 3.885 Å, and is controlled by the van der Waals distance between symmetry related chlorides in the polymer chain. Since this is the repeat translation in

the lattice, this distance is also the distance between corresponding atoms in the btzp planes within a given chain. The btzp planes are not directly face to face, but are offset so they slip-stack (a somewhat long π stacking distance) both within a polymer chain and also by interleaving btzp planes from adjacent chains (see figures below).

[1] SAINT, Bruker Analytical X-Ray Systems, Madison, WI, current version.

[2] An empirical correction for absorption anisotropy, Blessing, R., *Acta Cryst*. **1995**, *A51*, 33-38.

[3] Sir2004, A Program for Automatic Solution and Refinement of Crystal Structure. Burla, M. C.; Caliandro, R.; Carnalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Sagna. R., version 1.0 (2004).

[4] SHELXTL-Plus, Bruker Analytical X-Ray Systems, Madison, WI, current version.

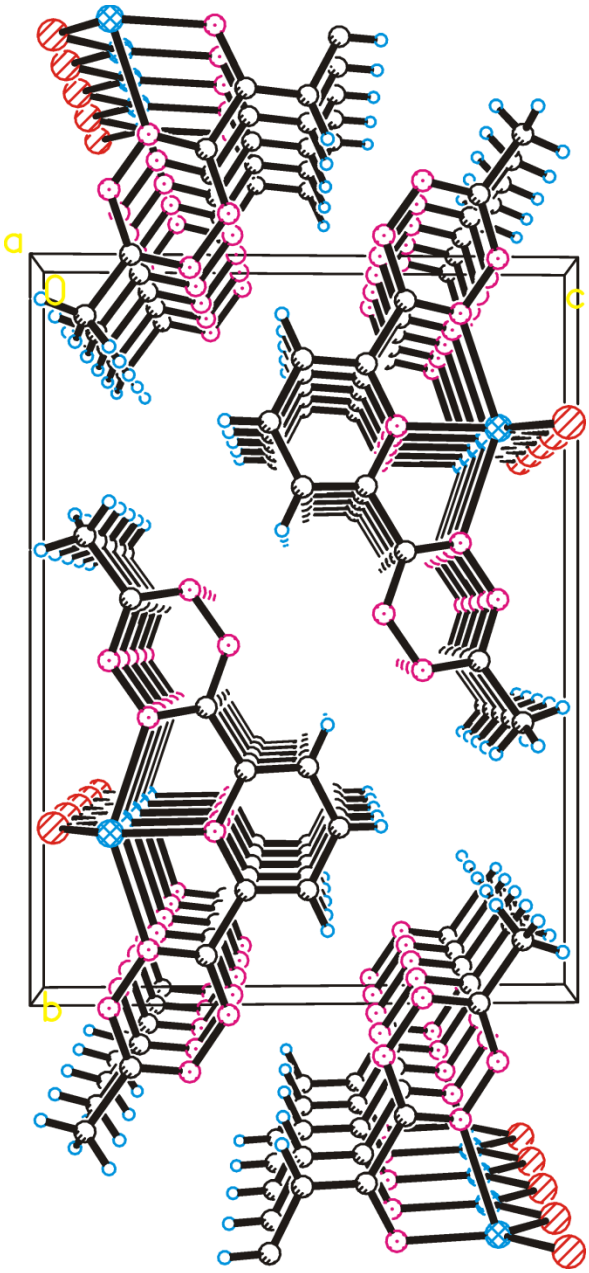

Figure S3. Cell plot, viewed along *a*- axis

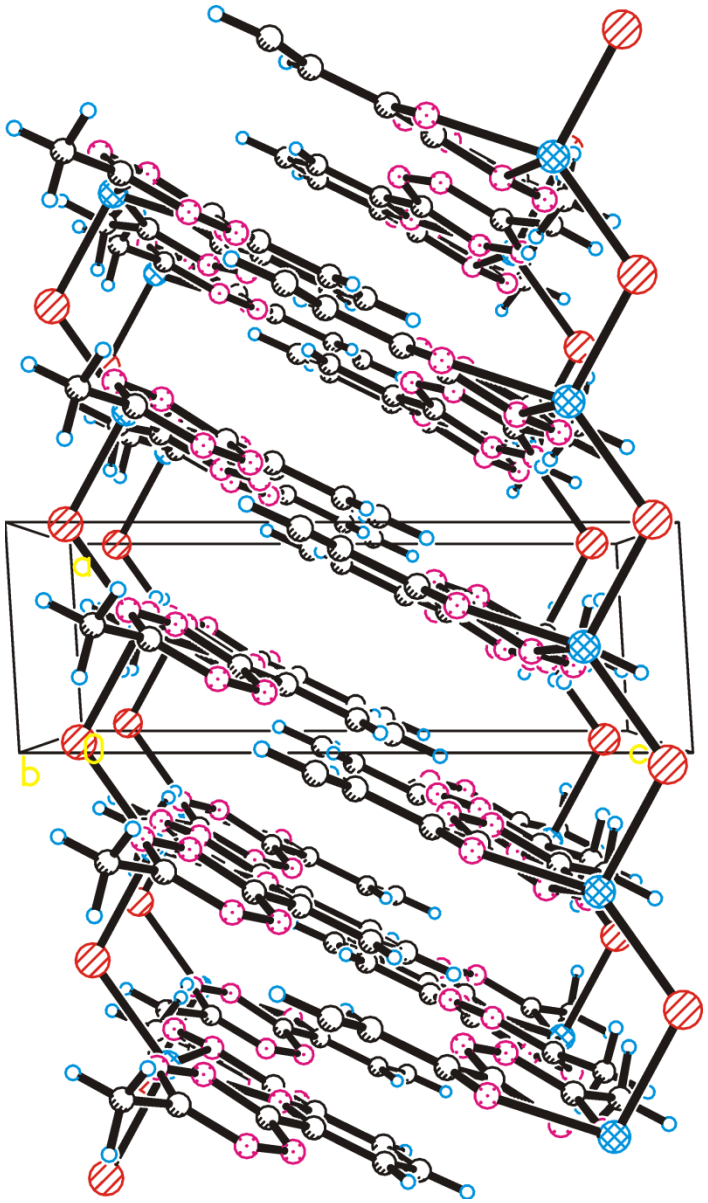

Figure S4. Cell plot, viewed along *b*- axis

Table Sa. Cartesian coordinates (Å) of all species.

[Cu(btzp)Cl]0 singlet

Cu	0.202352	-0.000009	-1.355915
Cl	1.582663	-0.000024	-3.063398
N	-0.019147	-0.000004	0.705830
O	-0.052230	-1.160957	1.375468
O	-0.052203	1.160952	1.375463
O	-0.068837	-1.207608	2.772368
O	-0.068815	1.207610	2.772363
O	-0.068059	0.000002	3.471693
H	-0.079773	-2.166441	3.276652
H	-0.079731	2.166445	3.276642
H	-0.077147	0.000005	4.556866
O	-0.073036	2.361173	0.513472
O	0.013140	4.392959	-1.055970
O	-0.073094	-2.361182	0.513482
O	0.013093	-4.392962	-1.055965
N	-0.354317	2.159483	-0.795052
N	-0.319128	3.205591	-1.596861
N	0.184550	4.608047	0.265055
N	0.133921	3.558997	1.067169
N	-0.354354	-2.159490	-0.795048
N	-0.319195	-3.205600	-1.596855
N	0.184451	-4.608060	0.265065
N	0.133924	-3.558999	1.067171
O	0.166405	-5.556668	-1.982090
H	-0.560265	-5.492158	-2.794517
H	1.165716	-5.537583	-2.432467
H	0.051594	-6.493223	-1.434743
O	0.166366	5.556683	-1.982086
H	1.165663	5.537638	-2.432496
H	-0.560329	5.492156	-2.794490
H	0.051541	6.493228	-1.434725

[Cu(btzp)Cl]0 triplet

Cu	0.000018	-0.860310	-0.000757
Cl	-0.000025	-3.064953	0.000159
N	0.000007	1.141370	-0.001602
O	-1.174826	1.801935	0.010261
O	1.174875	1.801892	-0.013908
O	-1.213742	3.195539	0.010157
O	1.213789	3.195529	-0.014813
O	0.000044	3.891788	-0.002588
H	-2.171359	3.702562	0.019836
H	2.171414	3.702532	-0.024834
H	0.000049	4.976718	-0.002983
O	2.326205	0.903525	-0.025377
O	4.280341	-0.776751	-0.044747
O	-2.326217	0.903581	0.022476
O	-4.280385	-0.776605	0.043264
N	2.036117	-0.428104	-0.021866
N	3.054594	-1.290687	-0.031968
N	4.578337	0.558010	-0.048373
N	3.562193	1.400985	-0.038281
N	-2.036154	-0.428037	0.020032
N	-3.054623	-1.290598	0.030877
N	-4.578345	0.558132	0.045804
N	-3.562165	1.401100	0.035015
O	-5.439045	-1.723752	0.055521
H	-5.080963	-2.753350	0.051357
H	-6.056176	-1.550659	0.942887
H	-6.075130	-1.550160	-0.818265
O	5.439019	-1.723870	-0.056175
H	5.080954	-2.753475	-0.051118
H	6.056111	-1.551512	-0.943712
H	6.075127	-1.549551	0.817455

[Cu(btzp)Cl]0 singlet @ oxidized (flat)

Cu	0.000000	-0.878807	-0.000013
Cl	-0.000002	-3.045462	-0.000038
N	0.000000	1.140562	0.000003
O	1.167722	1.796560	0.001233
O	-1.167722	1.796562	-0.001226
O	1.213665	3.192031	0.001440
O	-1.213663	3.192032	-0.001428
O	0.000001	3.886575	0.000008
H	2.169501	3.703180	0.002690
H	-2.169499	3.703183	-0.002680
H	0.000002	4.971648	0.000010
O	-2.341995	0.900092	-0.002142
O	-4.327486	-0.759178	-0.001645
O	2.341993	0.900089	0.002140
O	4.327483	-0.759182	0.001650
N	-2.086784	-0.421848	-0.001098
N	-3.078828	-1.272777	-0.000908
N	-4.589788	0.571988	-0.006533
N	-3.580923	1.409139	-0.005921
N	2.086782	-0.421849	0.001092
N	3.078827	-1.272780	0.000905
N	4.589786	0.571985	0.006492
N	3.580924	1.409136	0.005888
O	5.480708	-1.702109	-0.006923
H	5.131585	-2.728975	0.099396
H	6.033655	-1.600731	-0.947392
H	6.174115	-1.451680	0.801262
O	-5.480704	-1.702110	0.007040
H	-5.131680	-2.728874	-0.100603
H	-6.032705	-1.601734	0.948184
H	-6.174916	-1.450835	-0.800177

[Cu(btzp)Cl]+ doublet

Cu	-0.000002	0.878495	-0.000038
Cl	-0.000005	3.045150	-0.000407
N	-0.000001	-1.140874	0.000313
O	1.167722	-1.796872	0.000472
O	-1.167723	-1.796874	0.000392
O	1.213666	-3.192342	0.000568
O	-1.213664	-3.192345	0.000797
O	0.000001	-3.886887	0.000807
H	2.169503	-3.703491	0.000449
H	-2.169500	-3.703495	0.001103
H	0.000003	-4.971960	0.001002
O	-2.341997	-0.900406	-0.000132
O	-4.327487	0.758863	-0.003088
O	2.341993	-0.900400	0.000678
O	4.327480	0.758872	0.003024
N	-2.086786	0.421535	-0.001138
N	-3.078829	1.272463	-0.002561
N	-4.589793	-0.572302	0.001757
N	-3.580929	-1.409452	0.002394
N	2.086781	0.421538	0.001209
N	3.078824	1.272470	0.002319
N	4.589789	-0.572295	-0.001291
N	3.580927	-1.409447	-0.001631
O	5.480695	1.701802	0.012680
H	5.131687	2.728648	-0.094205
H	6.032620	1.600595	0.953767
H	6.174980	1.451227	-0.794706
O	-5.480696	1.701793	-0.013198
H	-5.131789	2.728576	0.094638
H	-6.031673	1.601245	-0.954923
H	-6.175784	1.450664	0.793310

[Cu(py)(dmt)2Cl]0 singlet

Cu	-0.036548	-0.190160	1.100998
Cl	-0.184138	-1.216052	3.266947
N	0.221967	1.869544	1.435978
O	0.280736	2.270313	2.720243
O	0.325580	2.796351	0.467427
O	0.444962	3.607532	3.075910
O	0.490990	4.152097	0.738308
O	0.552103	4.566203	2.069194
H	0.486669	3.883008	4.124440
H	0.569498	4.861856	-0.078627
H	0.680675	5.616115	2.315693
O	2.298397	-2.018261	1.041809
O	3.346753	-1.306284	-1.199640
O	-2.759187	-1.364381	1.014832
O	-3.589287	-0.373353	-1.211938
N	1.664777	-1.079419	0.315527
N	2.197994	-0.708053	-0.839068
N	3.962421	-2.272393	-0.492247
N	3.420616	-2.634065	0.661774
N	-1.905580	-0.608897	0.299909
N	-2.325280	-0.095756	-0.847048
N	-4.431103	-1.162475	-0.518314
N	-4.000400	-1.668691	0.628325
O	-4.096008	0.238655	-2.482140
H	-4.499561	1.237607	-2.280089
H	-3.284303	0.344566	-3.204433
H	-4.899130	-0.372579	-2.896529
O	3.987470	-0.865539	-2.480222
H	4.589890	-1.675301	-2.894807
H	3.227553	-0.548591	-3.196952
H	4.650195	-0.012979	-2.291793
H	0.189857	1.475969	3.457616
H	0.272291	2.429636	-0.553509
H	1.839326	-2.274846	1.993808
H	-2.382603	-1.741098	1.963066

[Cu(btzp)] doublet

N	0.005315	0.254774	0.070580
O	-1.157796	0.915059	0.037459
O	1.135166	0.967947	0.106601
O	-1.238929	2.319232	0.046471
O	1.160172	2.372935	0.109183
O	-0.052516	3.051851	0.079531
H	-2.203290	2.810430	-0.021932
H	2.109273	2.894251	0.128855
H	-0.075669	4.137323	0.072179
O	2.411482	0.201537	0.139014
N	2.370943	-1.109640	0.449253
N	3.503703	-1.778767	0.396463
O	4.621884	-1.112970	0.042460
O	-2.395553	0.095587	-0.001293
N	-3.487651	0.592288	0.648557
N	-4.657174	-0.092397	0.539534
O	-4.603865	-1.249915	-0.116891
N	-3.507412	-1.778547	-0.705408
N	-2.384647	-1.044545	-0.676850
N	3.540957	0.886005	-0.107032
N	4.676879	0.215783	-0.154913
O	5.885651	-1.901072	-0.108224
H	5.928853	-2.350735	-1.107208
H	6.752729	-1.249339	0.010033
H	5.914142	-2.713742	0.620521
O	-5.873997	-2.041545	-0.224087
H	-6.695636	-1.506978	0.254030
H	-6.115035	-2.226025	-1.275170
H	-5.745868	-3.018179	0.253428
Cu	-3.271642	1.595880	2.322200

Table Sb. Frequencies (cm^{-1}) for all fully optimized species.

[Cu(btzp)Cl]0 singlet

24.1950	36.3632	41.8953
46.6721	48.9035	58.9087
62.4770	76.8283	84.6857
109.1424	111.1349	150.3249
159.5139	173.1068	190.8749
258.4210	316.5704	327.0009
328.2873	353.9070	356.7012
357.6291	366.0848	379.5147
447.1908	467.1347	471.8718
549.5603	551.3776	627.0543
637.5638	674.7879	677.9505
682.3002	701.2097	763.9823
808.4607	811.0476	830.8073
856.3081	866.6291	883.2959
963.6853	991.4290	992.4317
1023.7401	1033.2608	1059.1595
1059.3228	1062.6596	1062.6648
1077.9288	1102.8363	1102.9139
1135.8122	1163.4197	1190.1758
1297.2621	1315.9345	1329.4666
1333.0546	1367.7527	1397.7293
1410.7158	1435.1902	1437.5377
1449.1866	1464.6358	1473.4856
1481.5328	1491.1277	1495.4817
1500.6512	1513.4882	1527.6125
1546.0641	1625.5680	1643.3864
3061.5314	3061.5322	3132.7725
3132.7812	3175.8930	3175.8993
3213.3556	3241.2361	3243.3930

[Cu(btzp)Cl]0 triplet

25.0347	54.9307	57.8173
74.5810	77.9852	84.0794
91.0012	93.9944	117.2906
175.6523	175.8881	177.9665
184.8210	196.6827	215.0621
278.7777	318.9428	328.5785
337.1104	347.6491	363.8182
377.8848	382.8318	387.7788
456.0922	473.6440	493.5617
556.8281	566.9734	619.4325
638.1047	669.4273	677.4295
681.3127	706.5066	748.6323
779.7101	792.0634	810.7473
844.2952	863.4667	866.8530
959.3285	997.7344	998.7788
1010.3829	1025.8150	1061.6289
1062.0213	1062.2926	1081.3864
1085.5563	1091.8873	1099.0947
1137.5951	1146.1763	1175.7289
1244.1169	1262.8695	1296.9235
1304.1553	1318.8847	1354.1204
1368.7822	1406.2284	1413.4708
1435.1641	1443.2827	1448.0175
1469.1176	1485.7200	1485.7599
1493.1845	1494.2013	1521.6459
1552.6851	1582.7537	1642.6151
3062.5554	3062.6210	3123.0556
3123.0772	3176.5920	3176.6453
3215.1408	3239.7050	3242.2663

[Cu(btzp)Cl]+ doublet

19.9746	20.8678	24.9649
51.2011	54.5164	72.1495
84.7066	87.7831	108.0225
146.3250	166.1217	172.9682
182.3129	190.2743	217.7379
272.8819	317.5880	324.6889
340.2165	355.7447	381.6326
383.3199	385.1668	399.0684
458.1005	472.3776	481.9915
545.6741	556.1419	619.9803
643.5221	676.5599	688.0689
688.3842	707.5732	769.5681
811.6885	818.5882	831.4579
865.4380	866.7832	881.8208
975.6725	985.7406	987.0086
1044.1727	1047.1895	1055.7568
1055.9634	1072.5444	1073.8525
1076.8501	1101.6455	1107.9302
1146.6096	1176.9748	1200.9255
1305.6386	1326.5518	1333.2779
1342.2496	1375.3774	1410.7579
1414.1866	1432.3906	1438.8871
1452.8311	1473.5932	1475.0507
1475.8755	1491.0268	1496.1398
1506.7285	1520.0602	1538.6887
1545.2645	1630.6963	1642.3761
3064.9545	3065.0010	3129.1476
3129.1664	3185.2997	3185.3078
3224.7264	3242.2635	3244.7230

[Cu(py)(dmt)2Cl]0 singlet

-16.2122	3.0526	10.9686
12.8814	20.5313	24.8110
29.3863	36.5002	73.7959
86.2619	93.9778	114.2330

117.8462	118.3924	122.6405
137.0551	157.5867	163.3262
172.1186	185.0962	187.2983
231.8666	360.6610	364.5994
374.6863	377.8249	397.6467
433.0051	455.8594	463.9505
607.8475	608.8785	638.8645
665.1800	674.1526	676.2392
716.8518	771.1754	807.0384
807.7157	865.5649	869.4670
900.6436	967.4233	988.1207
990.0193	994.7064	997.0334
1013.0303	1031.5889	1033.9823
1038.1636	1039.2891	1049.1460
1063.9545	1064.4631	1076.4039
1076.9177	1092.8938	1097.6746
1154.7420	1160.2338	1179.5170
1212.9163	1218.0678	1248.6884
1309.6060	1351.9116	1353.8054
1391.2854	1419.2762	1420.7009
1429.3452	1430.3250	1474.8211
1477.2882	1488.9278	1491.4576
1492.2243	1498.9960	1504.8358
1523.4265	1556.4742	1560.7899
1629.7751	1654.9602	3061.1034
3061.2114	3132.8778	3133.1153
3174.2517	3174.3914	3187.4719
3195.1032	3200.1728	3201.7192
3202.1898	3217.1020	3222.4394

[Cu(btzp)] doublet

21.4118	23.6932	34.9622
38.2515	50.0876	53.1980
55.7854	78.3147	97.3334
131.8048	162.4228	172.6172
222.3389	248.8191	309.2024
325.5614	333.3805	339.6618
342.4798	351.0782	382.3573
428.1116	438.5131	501.6778
514.6480	579.9275	620.2993
628.1603	667.0155	673.3024
685.9648	695.3974	761.6953
776.0634	807.3317	826.5615
852.7530	869.5619	881.5384
943.8845	980.6603	997.4727
1007.2607	1017.4412	1049.5015
1051.1110	1061.2060	1062.6204
1070.2108	1099.1186	1114.4218
1135.7939	1151.5030	1185.6290
1233.1070	1286.9248	1303.7642
1317.1962	1349.3417	1357.1493
1396.3861	1404.6693	1435.3938
1440.8819	1461.7129	1471.6861
1479.7330	1486.7967	1488.9276
1496.6850	1513.6368	1516.7073
1538.4261	1622.8636	1628.7340
3059.0066	3063.6138	3126.1596
3129.7180	3168.7572	3172.4165
3201.8248	3221.2466	3242.4401

Table Sc. Energies (E_h) for all species. One E(SCF) is reported for partially optimized structures.

Species	**E(SCF)**	**H(gas)**	**G(gas)**
$[Cu(btzp)Cl]^0$ singlet	-1573.640731	-1573.410305	-1573.485102
$[Cu(btzp)Cl]^0$ triplet	-1573.620729	-1573.391429	-1573.462930
$[Cu(btzp)Cl]^0$ singlet planar	-1573.618203	-	-
$[Cu(btzp)Cl]^+$ doublet	-1573.399007	-1573.167721	-1573.241932
$[Cu(py)(dmt)_2Cl]^0$ singlet	-1576.050488	-1575.775140	-1575.861905
$[Cu(btzp)]^0$ doublet	-1113.333049	-1113.106955	-1113.179836