Electronic Supplementary Information for Dalton Transactions

Electronic supplementary information (ESI)

Synthesis, characterization, and dioxygen reactivity of copper(I) complexes with glycoligands

Ziad Damaj, Federico Cisnetti, Laurent Dupont, Eric Henon, Clotilde Policar* Emmanuel Guillon*

Contents:

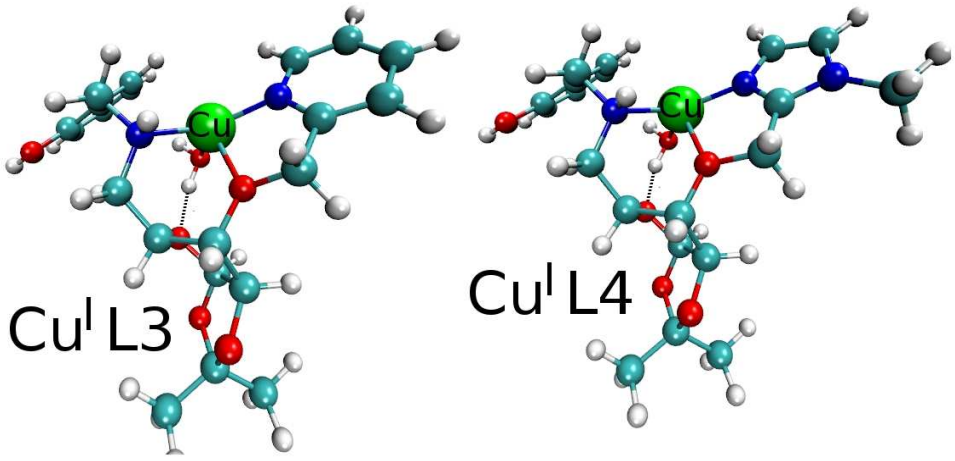

Fig.S1 Tetrahedral structures for Cu^{I}L3 and Cu^{I}L4; PCM HF-DFT (B3LYP)/6-31G* optimized geometries

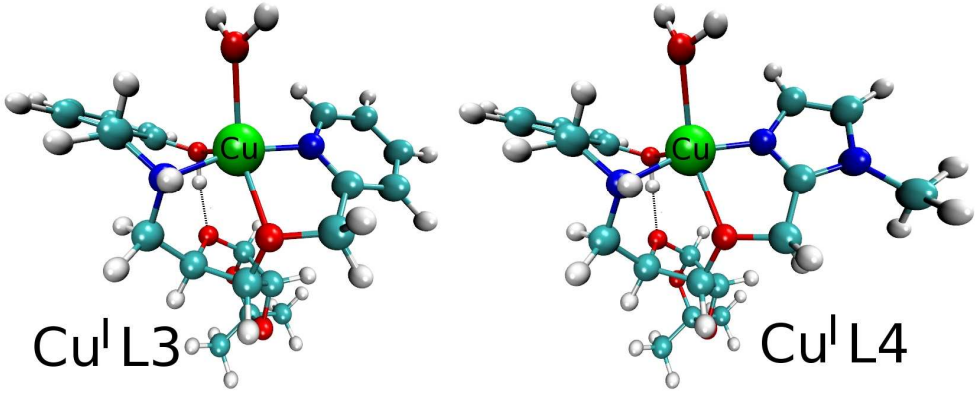

Fig. S2 Other possible pentacoordinate distorted square pyramidal structures for Cu^{I}L3 and Cu^{I}L4; PCM HF-DFT (B3LYP)/6-31G* optimized geometries

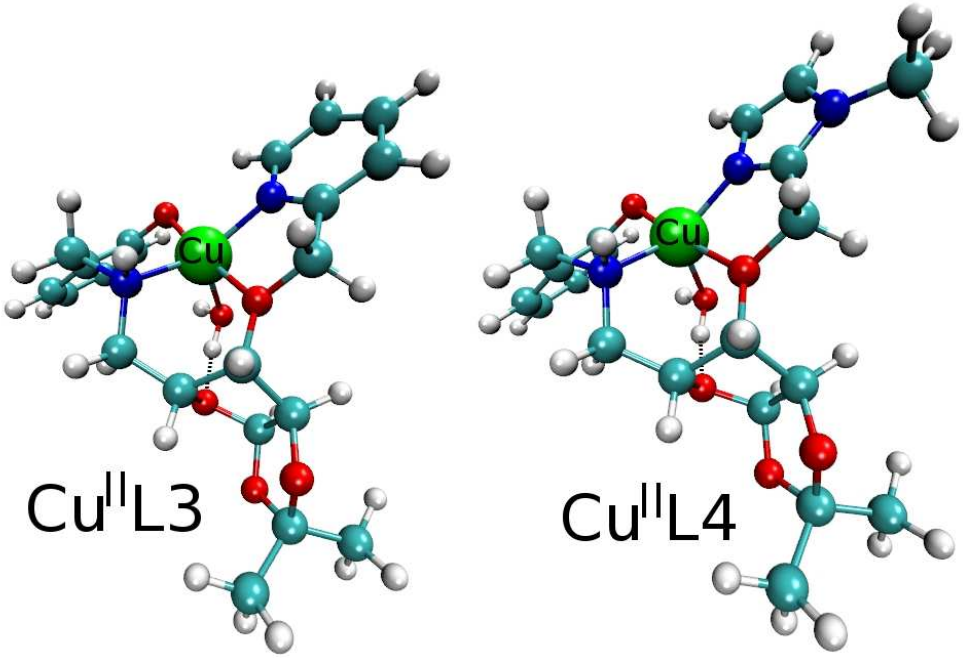

Fig. S3 Pentacoordinate distorted square pyramidal structures for Cu^{II}L3 and Cu^{II}L4; PCM HF-DFT (B3LYP)/6-31G*

Cu^{I}L1 HF-DFT (B3LYP)/6-31G*/PCM optimized structure

ZPE corrected energy = -2900.959580 hartree

(pdb format)

```
HEADER
HETATM    1 CU    2    2     -1.318   0.194   0.527
HETATM    2  N    2    2     -2.087  -1.480  -0.076
HETATM    3  N    2    2     -1.500   1.999  -0.100
HETATM    4  O    2    2     -0.984  -0.131   2.587
HETATM    5  H    2    2     -1.532  -0.739   3.105
HETATM    6  H    2    2     -0.071  -0.515   2.602
HETATM    7  C    2    2     -1.406  -2.240  -0.965
HETATM    8  C    2    2     -1.831  -3.510  -1.344
HETATM    9  C    2    2     -3.010  -4.022  -0.804
HETATM   10  C    2    2     -3.717  -3.244   0.111
HETATM   11  C    2    2     -3.220  -1.991   0.450
HETATM   12  C    2    2     -0.176  -1.597  -1.552
HETATM   13  H    2    2     -1.244  -4.086  -2.052
HETATM   14  H    2    2     -3.364  -5.008  -1.088
HETATM   15  H    2    2     -4.638  -3.598   0.562
HETATM   16  C    2    2     -0.550   2.935   0.126
HETATM   17  C    2    2     -0.596   4.199  -0.458
HETATM   18  C    2    2     -1.667   4.531  -1.285
HETATM   19  C    2    2     -2.659   3.577  -1.506
HETATM   20  C    2    2     -2.533   2.331  -0.906
HETATM   21  C    2    2      0.526   2.562   1.125
HETATM   22  H    2    2      0.197   4.913  -0.258
HETATM   23  H    2    2     -1.723   5.511  -1.749
HETATM   24  H    2    2     -3.514   3.785  -2.140
HETATM   25  H    2    2     -3.277   1.558  -1.065
HETATM   26  H    2    2     -3.747  -1.359   1.159
HETATM   27  O    2    2      0.518  -0.932  -0.494
HETATM   28  O    2    2      0.887   1.186   1.058
HETATM   29  H    2    2      1.404   3.208   1.006
HETATM   30  H    2    2      0.134   2.707   2.138
HETATM   31  H    2    2     -0.466  -0.856  -2.314
HETATM   32  H    2    2      0.458  -2.349  -2.035
HETATM   33  C    2    2      1.604  -0.118  -0.916
HETATM   34  C    2    2      1.994   0.822   0.252
HETATM   35  H    2    2      2.466   1.713  -0.173
HETATM   36  H    2    2      1.349   0.425  -1.833
HETATM   37  C    2    2      2.886  -0.946  -1.064
HETATM   38  C    2    2      3.057   0.003   1.054
HETATM   39  O    2    2      3.301  -1.185   0.273
HETATM   40  C    2    2      2.652  -0.450   2.452
HETATM   41  H    2    2      2.410   0.414   3.074
HETATM   42  O    2    2      1.505  -1.300   2.448
HETATM   43  H    2    2      3.503  -0.978   2.904
HETATM   44  H    2    2      1.596  -1.891   1.679
HETATM   45  O    2    2      3.787  -0.164  -1.788
HETATM   46  H    2    2      2.749  -1.936  -1.519
HETATM   47  C    2    2      5.046  -0.795  -2.027
HETATM   48  H    2    2      5.636  -0.093  -2.619
HETATM   49  H    2    2      5.565  -1.015  -1.088
HETATM   50  H    2    2      4.913  -1.727  -2.594
HETATM   51  H    2    2      3.986   0.581   1.136
```

$Cu^{I}L2$ HF-DFT (B3LYP)/6-31G*/PCM optimized structure

ZPE corrected energy = -2825.744659 hartree
(pdb format)

```
HEADER
HETATM    1  H     2    2      0.041   3.833   1.174
HETATM    2  C     2    2      0.640   3.169   0.541
HETATM    3  O     2    2      1.299   4.030  -0.384
HETATM    4  C     2    2      1.658   2.491   1.479
HETATM    5  C     2    2      2.007   3.364  -1.434
HETATM    6  C     2    2      1.061   2.519  -2.285
HETATM    7  H     2    2      2.459   4.163  -2.027
HETATM    8  H     2    2      2.819   2.745  -1.029
HETATM    9  C     2    2      0.300   1.513  -1.412
HETATM   10  H     2    2      0.333   3.175  -2.777
HETATM   11  H     2    2      1.613   2.003  -3.080
HETATM   12  C     2    2     -0.339   2.245  -0.223
HETATM   13  H     2    2     -0.494   1.021  -1.996
HETATM   14  O     2    2      1.149   0.501  -0.861
HETATM   15  H     2    2     -1.131   2.885  -0.631
HETATM   16  O     2    2     -0.895   1.296   0.688
HETATM   17  H     2    2      2.169   1.652   0.999
HETATM   18  H     2    2      2.396   3.260   1.731
HETATM   19  O     2    2      0.993   2.041   2.677
HETATM   20  H     2    2      1.608   2.149   3.419
HETATM   21  C     2    2      1.548  -0.533  -1.753
HETATM   22  C     2    2     -2.304   1.276   0.880
HETATM   23  C     2    2      2.025  -1.694  -0.920
HETATM   24  C     2    2      3.203  -2.380  -1.197
HETATM   25  C     2    2      3.561  -3.471  -0.405
HETATM   26  C     2    2      2.725  -3.829   0.652
HETATM   27  C     2    2      1.570  -3.088   0.872
HETATM   28  N     2    2      1.208  -2.039   0.104
HETATM   29  H     2    2      3.830  -2.059  -2.022
HETATM   30  H     2    2      4.474  -4.023  -0.606
HETATM   31  H     2    2      2.960  -4.666   1.300
HETATM   32  H     2    2      0.896  -3.341   1.685
HETATM   33  H     2    2     -2.463   1.123   1.954
HETATM   34  H     2    2     -2.757   2.237   0.608
HETATM   35  C     2    2     -2.954   0.139   0.117
HETATM   36  C     2    2     -4.275   0.210  -0.318
HETATM   37  C     2    2     -4.851  -0.900  -0.934
HETATM   38  C     2    2     -4.077  -2.048  -1.098
HETATM   39  C     2    2     -2.763  -2.037  -0.650
HETATM   40  N     2    2     -2.196  -0.967  -0.051
HETATM   41  H     2    2     -4.843   1.124  -0.173
HETATM   42  H     2    2     -5.879  -0.866  -1.282
HETATM   43  H     2    2     -4.478  -2.939  -1.571
HETATM   44  H     2    2     -2.125  -2.907  -0.770
HETATM   45 CU     2    2     -0.348  -0.982   0.505
HETATM   46  H     2    2      0.686  -0.844  -2.366
HETATM   47  H     2    2      2.341  -0.196  -2.432
HETATM   48  O     2    2     -0.110  -0.505   2.572
HETATM   49  H     2    2      0.397  -1.030   3.210
HETATM   50  H     2    2      0.239   0.419   2.635
```

$Cu^{I}L3$ HF-DFT (B3LYP)/6-31G*/PCM optimized structure

ZPE corrected energy = -3017.632633 hartree

Pentacoordinate distorted square pyramidal structure

(pdb format)

```
HEADER
HETATM    1 CU    2    2     -1.085   0.710  -0.012
HETATM    2  O    2    2      0.954   1.193   0.707
HETATM    3  N    2    2     -1.126   2.603  -0.085
HETATM    4  N    2    2     -1.015  -0.601   1.523
HETATM    5  O    2    2     -0.949  -0.482  -1.726
HETATM    6  H    2    2     -0.135  -0.997  -1.539
HETATM    7  H    2    2     -1.656  -1.137  -1.856
HETATM    8  C    2    2      1.446  -1.130   0.922
HETATM    9  O    2    2      1.423  -1.290  -0.516
HETATM   10  H    2    2      2.205  -1.812   1.325
HETATM   11  C    2    2      0.118  -1.565   1.544
HETATM   12  H    2    2     -0.194  -2.462   1.001
HETATM   13  C    2    2      2.605  -0.682  -1.044
HETATM   14  O    2    2      3.643  -1.607  -1.197
HETATM   15  H    2    2      2.325  -0.253  -2.009
HETATM   16  C    2    2      3.108   0.314   0.038
HETATM   17  O    2    2      4.268  -0.302   0.564
HETATM   18  H    2    2      3.312   1.318  -0.351
HETATM   19  C    2    2     -2.293  -1.275   1.927
HETATM   20  H    2    2     -2.116  -1.925   2.795
HETATM   21  H    2    2     -2.977  -0.480   2.233
HETATM   22  C    2    2     -2.901  -2.076   0.803
HETATM   23  C    2    2     -3.661  -1.433  -0.193
HETATM   24  C    2    2     -4.201  -2.157  -1.260
HETATM   25  C    2    2     -4.005  -3.538  -1.335
HETATM   26  C    2    2     -3.276  -4.197  -0.347
HETATM   27  C    2    2     -2.734  -3.462   0.710
HETATM   28  O    2    2     -3.849  -0.079  -0.067
HETATM   29  H    2    2     -4.789  -1.644  -2.020
HETATM   30  H    2    2     -4.434  -4.093  -2.164
HETATM   31  H    2    2     -3.131  -5.272  -0.393
HETATM   32  C    2    2     -2.153   3.290  -0.641
HETATM   33  C    2    2     -2.147   4.666  -0.817
HETATM   34  C    2    2     -1.025   5.391  -0.414
HETATM   35  C    2    2      0.038   4.698   0.160
HETATM   36  C    2    2     -0.046   3.317   0.320
HETATM   37  H    2    2     -3.006   2.696  -0.947
HETATM   38  H    2    2     -3.005   5.154  -1.267
HETATM   39  H    2    2     -0.977   6.467  -0.544
HETATM   40  H    2    2      0.930   5.223   0.490
HETATM   41  C    2    2      1.072   2.572   1.027
HETATM   42  H    2    2      2.044   2.977   0.721
HETATM   43  H    2    2      0.986   2.705   2.118
HETATM   44  C    2    2      1.991   0.298   1.094
HETATM   45  H    2    2      2.360   0.508   2.105
HETATM   46  H    2    2     -0.820   0.083   2.254
HETATM   47  C    2    2      4.789  -1.201  -0.424
HETATM   48  C    2    2      5.372  -2.413   0.280
HETATM   49  H    2    2      5.736  -3.135  -0.456
HETATM   50  H    2    2      6.208  -2.111   0.918
HETATM   51  H    2    2      4.609  -2.892   0.899
HETATM   52  C    2    2      5.791  -0.486  -1.329
HETATM   53  H    2    2      6.131  -1.161  -2.121
HETATM   54  H    2    2      5.334   0.391  -1.799
HETATM   55  H    2    2      6.658  -0.157  -0.748
HETATM   56  H    2    2      0.318  -1.873   2.581
HETATM   57  H    2    2     -2.179  -3.975   1.491
HETATM   58  H    2    2     -4.526   0.210  -0.701
```

Cu^{II}L3 HF-DFT (B3LYP)/6-31G*/PCM optimized structure

ZPE corrected energy = -3017.063997 hartree
hexacoordinate tetragonal (distorted octahedral) geometry
(pdb format)

```
HEADER
HETATM    1 CU    2    2     0.869   0.805  -0.514
HETATM    2  O    2    2    -0.855   0.836  -1.652
HETATM    3  N    2    2    -0.106   2.279   0.400
HETATM    4  N    2    2     1.524  -0.532  -1.835
HETATM    5  O    2    2     2.524   2.270  -1.683
HETATM    6  H    2    2     2.946   2.051  -0.826
HETATM    7  C    2    2    -0.725  -1.535  -1.255
HETATM    8  O    2    2    -0.468  -1.354   0.147
HETATM    9  H    2    2    -1.298  -2.457  -1.414
HETATM   10  C    2    2     0.611  -1.700  -1.971
HETATM   11  H    2    2     1.100  -2.563  -1.512
HETATM   12  C    2    2    -1.703  -1.031   0.774
HETATM   13  O    2    2    -2.404  -2.177   1.165
HETATM   14  H    2    2    -1.458  -0.407   1.636
HETATM   15  C    2    2    -2.586  -0.384  -0.333
HETATM   16  O    2    2    -3.613  -1.323  -0.567
HETATM   17  H    2    2    -2.987   0.598  -0.056
HETATM   18  C    2    2     2.962  -0.908  -1.606
HETATM   19  H    2    2     3.242  -1.714  -2.295
HETATM   20  H    2    2     3.533  -0.017  -1.883
HETATM   21  C    2    2     3.236  -1.306  -0.182
HETATM   22  C    2    2     3.814  -2.540   0.131
HETATM   23  C    2    2     4.131  -2.876   1.448
HETATM   24  C    2    2     3.859  -1.961   2.468
HETATM   25  C    2    2     3.268  -0.733   2.179
HETATM   26  C    2    2     2.945  -0.386   0.857
HETATM   27  H    2    2     4.032  -3.240  -0.673
HETATM   28  H    2    2     4.583  -3.837   1.673
HETATM   29  H    2    2     4.102  -2.208   3.498
HETATM   30  H    2    2     3.052  -0.017   2.967
HETATM   31  C    2    2     0.276   2.817   1.571
HETATM   32  C    2    2    -0.420   3.869   2.156
HETATM   33  C    2    2    -1.546   4.372   1.505
HETATM   34  C    2    2    -1.941   3.811   0.289
HETATM   35  C    2    2    -1.192   2.762  -0.237
HETATM   36  H    2    2     1.164   2.376   2.012
HETATM   37  H    2    2    -0.084   4.280   3.102
HETATM   38  H    2    2    -2.115   5.189   1.937
HETATM   39  H    2    2    -2.813   4.181  -0.241
HETATM   40  C    2    2    -1.491   2.126  -1.581
HETATM   41  H    2    2    -2.564   2.042  -1.770
HETATM   42  H    2    2    -1.053   2.724  -2.388
HETATM   43  C    2    2    -1.670  -0.361  -1.573
HETATM   44  H    2    2    -2.232  -0.474  -2.503
HETATM   45  H    2    2     1.496   0.005  -2.702
HETATM   46  O    2    2     2.393   0.815   0.591
HETATM   47  C    2    2    -3.723  -2.170   0.591
HETATM   48  C    2    2    -4.076  -3.574   0.133
HETATM   49  H    2    2    -4.120  -4.247   0.994
HETATM   50  H    2    2    -5.051  -3.572  -0.361
HETATM   51  H    2    2    -3.323  -3.944  -0.567
HETATM   52  C    2    2    -4.723  -1.588   1.587
HETATM   53  H    2    2    -4.755  -2.203   2.491
HETATM   54  H    2    2    -4.440  -0.570   1.876
HETATM   55  H    2    2    -5.723  -1.556   1.144
HETATM   56  H    2    2     0.437  -1.932  -3.028
HETATM   57  H    2    2     2.767   3.187  -1.887
```

$Cu^{I}L4$ HF-DFT (B3LYP)/6-31G*/PCM optimized structure

ZPE corrected energy = -3034.867246 hartree

Pentacoordinate distorted square pyramidal structure

(pdb format)

```
HEADER
HETATM    1  C    2    2      5.522  -1.631  -1.307
HETATM    2  C    2    2      4.419  -2.097  -0.357
HETATM    3  C    2    2      4.788  -3.346   0.425
HETATM    4  H    2    2      3.959  -3.641   1.074
HETATM    5  H    2    2      5.672  -3.156   1.041
HETATM    6  H    2    2      5.009  -4.167  -0.262
HETATM    7  H    2    2      5.729  -2.404  -2.052
HETATM    8  H    2    2      6.440  -1.423  -0.748
HETATM    9  H    2    2      5.222  -0.719  -1.834
HETATM   10  O    2    2      3.212  -2.344  -1.102
HETATM   11  O    2    2      4.077  -1.059   0.570
HETATM   12  C    2    2      3.035  -0.285   0.006
HETATM   13  H    2    2      3.410   0.637  -0.451
HETATM   14  C    2    2      2.354  -1.242  -1.010
HETATM   15  H    2    2      2.147  -0.832  -2.001
HETATM   16  C    2    2      1.955  -0.043   1.076
HETATM   17  H    2    2      2.391   0.121   2.069
HETATM   18  O    2    2      1.079   1.013   0.703
HETATM   19  C    2    2      1.532   2.354   0.781
HETATM   20  H    2    2      1.696   2.645   1.831
HETATM   21  H    2    2      2.486   2.496   0.251
HETATM   22  C    2    2      0.441   3.174   0.145
HETATM   23  N    2    2      0.480   4.526   0.006
HETATM   24  C    2    2      1.567   5.409   0.415
HETATM   25  H    2    2      1.269   6.440   0.227
HETATM   26  H    2    2      2.477   5.196  -0.155
HETATM   27  C    2    2     -0.697   4.905  -0.609
HETATM   28  H    2    2     -0.910   5.939  -0.835
HETATM   29  C    2    2     -1.407   3.757  -0.819
HETATM   30  H    2    2     -2.376   3.640  -1.278
HETATM   31  N    2    2     -0.691   2.673  -0.346
HETATM   32 CU    2    2     -1.093   0.825  -0.259
HETATM   33  C    2    2      1.142  -1.347   0.976
HETATM   34  H    2    2      1.749  -2.139   1.435
HETATM   35  O    2    2      1.091  -1.595  -0.447
HETATM   36  H    2    2     -0.345  -1.150  -1.541
HETATM   37  O    2    2     -1.047  -0.539  -1.853
HETATM   38  H    2    2     -1.834  -1.091  -1.993
HETATM   39  C    2    2     -0.248  -1.461   1.602
HETATM   40  H    2    2     -0.713  -2.348   1.161
HETATM   41  H    2    2     -0.113  -1.673   2.674
HETATM   42  N    2    2     -1.183  -0.321   1.427
HETATM   43  C    2    2     -2.553  -0.686   1.905
HETATM   44  C    2    2     -3.314  -1.490   0.882
HETATM   45  C    2    2     -3.838  -0.853  -0.258
HETATM   46  O    2    2     -3.639   0.505  -0.359
HETATM   47  C    2    2     -4.527  -1.575  -1.234
HETATM   48  C    2    2     -4.710  -2.952  -1.076
HETATM   49  C    2    2     -4.210  -3.601   0.051
HETATM   50  C    2    2     -3.518  -2.866   1.017
HETATM   51  H    2    2     -3.136  -3.367   1.903
HETATM   52  H    2    2     -4.356  -4.669   0.180
HETATM   53  H    2    2     -5.251  -3.507  -1.836
HETATM   54  H    2    2     -4.934  -1.063  -2.104
HETATM   55  H    2    2     -2.495  -1.243   2.851
HETATM   56  H    2    2     -3.071   0.257   2.101
HETATM   57  H    2    2     -0.849   0.419   2.044
HETATM   58  H    2    2     -4.173   0.857  -1.089
HETATM   59  H    2    2      1.773   5.295   1.484
```

$Cu^{II}L4$ HF-DFT (B3LYP)/6-31G*/PCM optimized structure

ZPE corrected energy = -3034.296723 hartree
hexacoordinate tetragonal (distorted octahedral) geometry
(pdb format)

```
HEADER
HETATM    1 CU    2    2      0.755   0.899  -0.300
HETATM    2 O     2    2     -0.998   0.752  -1.515
HETATM    3 N     2    2     -0.465   2.088   0.670
HETATM    4 N     2    2      1.606  -0.098  -1.798
HETATM    5 O     2    2      2.116   2.803  -1.408
HETATM    6 H     2    2      2.180   3.768  -1.462
HETATM    7 H     2    2      2.541   2.544  -0.562
HETATM    8 C     2    2     -0.395  -1.566  -1.334
HETATM    9 O     2    2     -0.133  -1.453   0.077
HETATM   10 H     2    2     -0.777  -2.568  -1.564
HETATM   11 C     2    2      0.928  -1.393  -2.074
HETATM   12 H     2    2      1.583  -2.194  -1.723
HETATM   13 C     2    2     -1.388  -1.437   0.749
HETATM   14 O     2    2     -1.833  -2.730   1.046
HETATM   15 H     2    2     -1.244  -0.849   1.658
HETATM   16 C     2    2     -2.416  -0.890  -0.284
HETATM   17 O     2    2     -3.245  -1.993  -0.584
HETATM   18 H     2    2     -2.993  -0.036   0.087
HETATM   19 C     2    2      3.099  -0.215  -1.649
HETATM   20 H     2    2      3.492  -0.878  -2.429
HETATM   21 H     2    2      3.479   0.792  -1.843
HETATM   22 C     2    2      3.507  -0.695  -0.283
HETATM   23 C     2    2      4.320  -1.819  -0.117
HETATM   24 C     2    2      4.751  -2.217   1.149
HETATM   25 C     2    2      4.354  -1.479   2.267
HETATM   26 C     2    2      3.529  -0.365   2.125
HETATM   27 C     2    2      3.092   0.045   0.854
HETATM   28 H     2    2      4.632  -2.381  -0.996
HETATM   29 H     2    2      5.385  -3.091   1.261
HETATM   30 H     2    2      4.683  -1.777   3.260
HETATM   31 H     2    2      3.212   0.213   2.988
HETATM   32 C     2    2     -0.421   2.824   1.832
HETATM   33 C     2    2     -1.518   3.639   1.874
HETATM   34 N     2    2     -2.241   3.393   0.717
HETATM   35 C     2    2     -1.567   2.451   0.019
HETATM   36 H     2    2      0.386   2.708   2.539
HETATM   37 H     2    2     -1.855   4.355   2.608
HETATM   38 C     2    2     -3.460   4.092   0.309
HETATM   39 C     2    2     -1.878   1.878  -1.338
HETATM   40 H     2    2     -2.925   1.580  -1.451
HETATM   41 H     2    2     -1.642   2.590  -2.138
HETATM   42 C     2    2     -1.563  -0.582  -1.531
HETATM   43 H     2    2     -2.121  -0.728  -2.460
HETATM   44 H     2    2      1.437   0.534  -2.581
HETATM   45 O     2    2      2.313   1.136   0.729
HETATM   46 C     2    2     -3.147  -2.937   0.498
HETATM   47 C     2    2     -3.234  -4.341  -0.074
HETATM   48 H     2    2     -3.120  -5.077   0.727
HETATM   49 H     2    2     -4.206  -4.490  -0.552
HETATM   50 H     2    2     -2.446  -4.497  -0.814
HETATM   51 C     2    2     -4.206  -2.648   1.559
HETATM   52 H     2    2     -4.085  -3.330   2.405
HETATM   53 H     2    2     -4.118  -1.622   1.932
HETATM   54 H     2    2     -5.208  -2.779   1.139
HETATM   55 H     2    2     -4.036   4.348   1.200
HETATM   56 H     2    2     -3.215   5.006  -0.240
HETATM   57 H     2    2     -4.068   3.441  -0.323
HETATM   58 H     2    2      0.773  -1.530  -3.150
```

$Cu^{I}L3$ HF-DFT (B3LYP)/6-31G*/PCM optimized structure
ZPE corrected energy = -3017.631920 hartree
distorted tetrahedral geometry
(pdb format)

```
HEADER
HETATM    1 CU    2    2      0.982   0.992  -0.019
HETATM    2  O    2    2     -1.059   1.160  -0.729
HETATM    3  N    2    2      0.789   2.880   0.033
HETATM    4  N    2    2      1.164  -0.374  -1.480
HETATM    5  O    2    2      1.049  -0.090   1.773
HETATM    6  H    2    2      0.361  -0.770   1.619
HETATM    7  H    2    2      1.884  -0.572   1.904
HETATM    8  C    2    2     -1.206  -1.218  -0.878
HETATM    9  O    2    2     -1.159  -1.323   0.564
HETATM   10  H    2    2     -1.862  -2.014  -1.255
HETATM   11  C    2    2      0.168  -1.484  -1.494
HETATM   12  H    2    2      0.593  -2.332  -0.955
HETATM   13  C    2    2     -2.419  -0.882   1.075
HETATM   14  O    2    2     -3.309  -1.947   1.252
HETATM   15  H    2    2     -2.211  -0.390   2.027
HETATM   16  C    2    2     -3.061  -0.002  -0.035
HETATM   17  O    2    2     -4.121  -0.791  -0.537
HETATM   18  H    2    2     -3.405   0.976   0.323
HETATM   19  C    2    2      2.543  -0.882  -1.793
HETATM   20  H    2    2      2.503  -1.591  -2.628
HETATM   21  H    2    2      3.117  -0.009  -2.117
HETATM   22  C    2    2      3.220  -1.508  -0.598
HETATM   23  C    2    2      3.862  -0.703   0.352
HETATM   24  C    2    2      4.475  -1.244   1.483
HETATM   25  C    2    2      4.463  -2.630   1.667
HETATM   26  C    2    2      3.849  -3.456   0.728
HETATM   27  C    2    2      3.231  -2.900  -0.399
HETATM   28  H    2    2      3.895   0.372   0.184
HETATM   29  H    2    2      4.976  -0.598   2.198
HETATM   30  H    2    2      4.939  -3.072   2.537
HETATM   31  H    2    2      3.844  -4.535   0.867
HETATM   32  C    2    2      1.681   3.719   0.611
HETATM   33  C    2    2      1.458   5.079   0.768
HETATM   34  C    2    2      0.253   5.620   0.323
HETATM   35  C    2    2     -0.676   4.768  -0.269
HETATM   36  C    2    2     -0.378   3.415  -0.407
HETATM   37  H    2    2      2.605   3.267   0.954
HETATM   38  H    2    2      2.217   5.697   1.238
HETATM   39  H    2    2      0.038   6.678   0.435
HETATM   40  H    2    2     -1.629   5.147  -0.627
HETATM   41  C    2    2     -1.350   2.495  -1.123
HETATM   42  H    2    2     -2.382   2.772  -0.875
HETATM   43  H    2    2     -1.232   2.589  -2.215
HETATM   44  C    2    2     -1.952   0.110  -1.093
HETATM   45  H    2    2     -2.341   0.238  -2.110
HETATM   46  H    2    2      0.916   0.233  -2.263
HETATM   47  C    2    2     -4.505  -1.728   0.478
HETATM   48  C    2    2     -4.913  -3.030  -0.190
HETATM   49  H    2    2     -5.166  -3.776   0.568
HETATM   50  H    2    2     -5.786  -2.867  -0.827
HETATM   51  H    2    2     -4.091  -3.412  -0.802
HETATM   52  C    2    2     -5.595  -1.139   1.372
HETATM   53  H    2    2     -5.832  -1.834   2.184
HETATM   54  H    2    2     -5.265  -0.194   1.816
HETATM   55  H    2    2     -6.502  -0.952   0.790
HETATM   56  H    2    2      0.014  -1.821  -2.529
HETATM   57  O    2    2      2.605  -3.675  -1.337
HETATM   58  H    2    2      2.721  -4.613  -1.114
```

$Cu^{I}L4$ HF-DFT (B3LYP)/6-31G*/PCM optimized structure

ZPE corrected energy = -3034.866598 hartree
distorted tetrahedral geometry
(pdb format)

```
HEADER
HETATM    1  H    2    2     -3.986  -3.607   1.434
HETATM    2  O    2    2     -3.608  -2.724   1.573
HETATM    3  C    2    2     -3.990  -1.896   0.552
HETATM    4  C    2    2     -4.748  -2.358  -0.532
HETATM    5  H    2    2     -5.054  -3.401  -0.568
HETATM    6  C    2    2     -5.101  -1.486  -1.558
HETATM    7  H    2    2     -5.690  -1.855  -2.393
HETATM    8  C    2    2     -4.711  -0.144  -1.508
HETATM    9  H    2    2     -5.007   0.546  -2.293
HETATM   10  C    2    2     -3.962   0.305  -0.420
HETATM   11  H    2    2     -3.673   1.353  -0.359
HETATM   12  C    2    2     -3.579  -0.554   0.619
HETATM   13  C    2    2     -2.741  -0.031   1.761
HETATM   14  H    2    2     -2.890  -0.641   2.660
HETATM   15  H    2    2     -3.048   0.993   1.993
HETATM   16  N    2    2     -1.284   0.045   1.416
HETATM   17  O    2    2     -1.138  -0.019  -1.884
HETATM   18  H    2    2     -2.078  -0.238  -2.011
HETATM   19  H    2    2     -0.698  -0.854  -1.626
HETATM   20  C    2    2     -0.621  -1.279   1.580
HETATM   21  H    2    2     -0.537  -1.522   2.649
HETATM   22  H    2    2     -1.268  -2.042   1.141
HETATM   23  C    2    2      0.758  -1.460   0.948
HETATM   24  O    2    2      0.647  -1.637  -0.482
HETATM   25  H    2    2      1.168  -2.384   1.376
HETATM   26  C    2    2      1.958  -1.586  -1.039
HETATM   27  H    2    2      1.859  -1.118  -2.021
HETATM   28  O    2    2      2.526  -2.861  -1.154
HETATM   29  C    2    2      3.765  -2.919  -0.424
HETATM   30  O    2    2      3.683  -1.851   0.529
HETATM   31  C    2    2      4.937  -2.701  -1.379
HETATM   32  H    2    2      4.853  -1.733  -1.884
HETATM   33  H    2    2      5.883  -2.725  -0.829
HETATM   34  H    2    2      4.952  -3.485  -2.142
HETATM   35  H    2    2      4.749  -4.272   0.935
HETATM   36  C    2    2      3.839  -4.236   0.329
HETATM   37  H    2    2      2.971  -4.344   0.984
HETATM   38  H    2    2      3.856  -5.071  -0.377
HETATM   39  C    2    2      2.847  -0.842  -0.004
HETATM   40  H    2    2      3.423  -0.019  -0.440
HETATM   41  H    2    2      2.315  -0.356   2.076
HETATM   42  C    2    2      1.855  -0.386   1.081
HETATM   43  O    2    2      1.256   0.861   0.740
HETATM   44 CU    2    2     -0.785   1.161  -0.184
HETATM   45  H    2    2     -0.863   0.656   2.115
HETATM   46  C    2    2      2.012   2.058   0.863
HETATM   47  H    2    2      2.994   1.973   0.376
HETATM   48  H    2    2      2.190   2.289   1.925
HETATM   49  C    2    2      1.174   3.117   0.197
HETATM   50  N    2    2     -0.044   2.903  -0.299
HETATM   51  N    2    2      1.548   4.412   0.032
HETATM   52  C    2    2      2.819   5.007   0.435
HETATM   53  C    2    2      0.507   5.057  -0.608
HETATM   54  H    2    2      0.559   6.106  -0.857
HETATM   55  C    2    2     -0.465   4.118  -0.806
HETATM   56  H    2    2     -1.430   4.232  -1.276
HETATM   57  H    2    2      2.776   6.080   0.248
HETATM   58  H    2    2      2.996   4.845   1.502
HETATM   59  H    2    2      3.646   4.581  -0.141
```

$Cu^{I}L3$ HF-DFT (B3LYP)/6-31G*/PCM optimized structure

ZPE corrected energy = -3017.622645 hartree
other pentacoordinate distorted square pyramidal structure
(pdb format)

```
HEADER
HETATM    1 CU    2    2     0.863   1.214  -0.324
HETATM    2  O    2    2    -1.060   0.713  -1.634
HETATM    3  N    2    2    -0.323   2.609   0.179
HETATM    4  N    2    2     1.488  -0.165  -1.676
HETATM    5  O    2    2     2.619   2.731  -0.452
HETATM    6  H    2    2     3.501   2.822  -0.054
HETATM    7  C    2    2    -0.605  -1.581  -1.180
HETATM    8  O    2    2    -0.501  -1.497   0.260
HETATM    9  H    2    2    -0.989  -2.576  -1.440
HETATM   10  C    2    2     0.785  -1.473  -1.804
HETATM   11  H    2    2     1.402  -2.233  -1.315
HETATM   12  C    2    2    -1.793  -1.248   0.814
HETATM   13  O    2    2    -2.420  -2.424   1.233
HETATM   14  H    2    2    -1.641  -0.575   1.661
HETATM   15  C    2    2    -2.663  -0.709  -0.349
HETATM   16  O    2    2    -3.547  -1.776  -0.639
HETATM   17  H    2    2    -3.202   0.210  -0.093
HETATM   18  C    2    2     2.963  -0.327  -1.613
HETATM   19  H    2    2     3.329  -0.903  -2.476
HETATM   20  H    2    2     3.375   0.684  -1.706
HETATM   21  C    2    2     3.493  -0.979  -0.347
HETATM   22  C    2    2     4.699  -1.692  -0.444
HETATM   23  C    2    2     5.315  -2.254   0.671
HETATM   24  C    2    2     4.722  -2.122   1.927
HETATM   25  C    2    2     3.519  -1.431   2.050
HETATM   26  C    2    2     2.910  -0.868   0.927
HETATM   27  H    2    2     5.162  -1.802  -1.422
HETATM   28  H    2    2     6.249  -2.797   0.557
HETATM   29  H    2    2     5.189  -2.557   2.806
HETATM   30  H    2    2     3.031  -1.315   3.013
HETATM   31  C    2    2    -0.035   3.390   1.246
HETATM   32  C    2    2    -0.955   4.249   1.833
HETATM   33  C    2    2    -2.247   4.310   1.312
HETATM   34  C    2    2    -2.554   3.516   0.207
HETATM   35  C    2    2    -1.575   2.689  -0.338
HETATM   36  H    2    2     0.981   3.322   1.617
HETATM   37  H    2    2    -0.661   4.851   2.686
HETATM   38  H    2    2    -2.997   4.961   1.750
HETATM   39  H    2    2    -3.544   3.543  -0.239
HETATM   40  C    2    2    -1.831   1.910  -1.615
HETATM   41  H    2    2    -2.900   1.719  -1.754
HETATM   42  H    2    2    -1.492   2.509  -2.471
HETATM   43  C    2    2    -1.696  -0.555  -1.539
HETATM   44  H    2    2    -2.209  -0.802  -2.476
HETATM   45  H    2    2     1.284   0.357  -2.526
HETATM   46  O    2    2     1.708  -0.179   1.131
HETATM   47  H    2    2     0.958  -0.811   1.033
HETATM   48  C    2    2    -3.660  -2.607   0.522
HETATM   49  C    2    2    -3.773  -4.054   0.076
HETATM   50  H    2    2    -3.812  -4.713   0.948
HETATM   51  H    2    2    -4.684  -4.196  -0.513
HETATM   52  H    2    2    -2.908  -4.326  -0.535
HETATM   53  C    2    2    -4.824  -2.152   1.402
HETATM   54  H    2    2    -4.859  -2.747   2.318
HETATM   55  H    2    2    -4.710  -1.099   1.681
HETATM   56  H    2    2    -5.771  -2.269   0.867
HETATM   57  H    2    2     0.708  -1.762  -2.861
HETATM   58  H    2    2     2.454   3.575  -0.902
```

$Cu^{I}L4$ HF-DFT (B3LYP)/6-31G*/PCM optimized structure

ZPE corrected energy = -3034.858171 hartree
other pentacoordinate distorted square pyramidal structure
(pdb format)

```
HEADER
HETATM    1 CU    2    2     -0.930   1.272  -0.015
HETATM    2  O    2    2      1.232   0.774   1.003
HETATM    3  N    2    2      0.189   2.737  -0.444
HETATM    4  N    2    2     -1.392   0.063   1.587
HETATM    5  O    2    2     -2.693   2.814   0.194
HETATM    6  H    2    2     -2.376   3.682   0.491
HETATM    7  C    2    2      0.613  -1.515   1.213
HETATM    8  O    2    2      0.403  -1.718  -0.204
HETATM    9  H    2    2      0.984  -2.456   1.642
HETATM   10  C    2    2     -0.715  -1.225   1.903
HETATM   11  H    2    2     -1.389  -2.037   1.613
HETATM   12  C    2    2      1.671  -1.709  -0.862
HETATM   13  O    2    2      2.174  -2.999  -1.049
HETATM   14  H    2    2      1.517  -1.216  -1.824
HETATM   15  C    2    2      2.660  -1.022   0.115
HETATM   16  O    2    2      3.463  -2.085   0.596
HETATM   17  H    2    2      3.262  -0.241  -0.363
HETATM   18  C    2    2     -2.870  -0.068   1.619
HETATM   19  H    2    2     -3.208  -0.498   2.574
HETATM   20  H    2    2     -3.258   0.954   1.571
HETATM   21  C    2    2     -3.464  -0.893   0.489
HETATM   22  C    2    2     -4.663  -1.578   0.743
HETATM   23  C    2    2     -5.331  -2.289  -0.251
HETATM   24  C    2    2     -4.799  -2.339  -1.540
HETATM   25  C    2    2     -3.603  -1.681  -1.815
HETATM   26  C    2    2     -2.941  -0.968  -0.814
HETATM   27  H    2    2     -5.078  -1.545   1.748
HETATM   28  H    2    2     -6.258  -2.804  -0.017
HETATM   29  H    2    2     -5.307  -2.891  -2.325
HETATM   30  H    2    2     -3.161  -1.705  -2.806
HETATM   31  C    2    2     -0.051   3.858  -1.219
HETATM   32  C    2    2      1.041   4.679  -1.186
HETATM   33  N    2    2      1.973   4.054  -0.381
HETATM   34  C    2    2      1.418   2.887   0.043
HETATM   35  H    2    2     -0.980   3.984  -1.752
HETATM   36  H    2    2      1.245   5.630  -1.656
HETATM   37  C    2    2      3.300   4.557  -0.042
HETATM   38  C    2    2      2.093   1.899   0.956
HETATM   39  H    2    2      3.091   1.643   0.575
HETATM   40  H    2    2      2.230   2.313   1.968
HETATM   41  C    2    2      1.777  -0.510   1.269
HETATM   42  H    2    2      2.312  -0.536   2.226
HETATM   43  H    2    2     -1.139   0.714   2.328
HETATM   44  O    2    2     -1.749  -0.325  -1.172
HETATM   45  H    2    2     -0.998  -0.939  -0.987
HETATM   46  C    2    2      3.438  -3.143  -0.370
HETATM   47  C    2    2      3.463  -4.472   0.365
HETATM   48  H    2    2      3.399  -5.297  -0.350
HETATM   49  H    2    2      4.394  -4.570   0.931
HETATM   50  H    2    2      2.618  -4.535   1.056
HETATM   51  C    2    2      4.577  -2.985  -1.375
HETATM   52  H    2    2      4.508  -3.757  -2.147
HETATM   53  H    2    2      4.530  -2.007  -1.865
HETATM   54  H    2    2      5.543  -3.074  -0.870
HETATM   55  H    2    2      3.455   5.506  -0.557
HETATM   56  H    2    2      3.388   4.723   1.035
HETATM   57  H    2    2      4.073   3.853  -0.366
HETATM   58  H    2    2     -0.560  -1.319   2.987
HETATM   59  H    2    2     -3.587   2.972  -0.152
```

$Cu^{II}L3$ HF-DFT (B3LYP)/6-31G*/PCM optimized structure

ZPE corrected energy = -3017.065546 hartree

pentacoordinate distorted square pyramidal structure

(pdb format)

```
HEADER
HETATM    1 CU    2    2    -1.208   0.444   0.166
HETATM    2 O     2    2     0.734   1.120   0.561
HETATM    3 N     2    2    -1.462   2.424   0.005
HETATM    4 N     2    2    -0.854  -0.905   1.654
HETATM    5 O     2    2    -0.642  -0.418  -1.758
HETATM    6 H     2    2     0.110  -1.019  -1.577
HETATM    7 H     2    2    -1.372  -0.967  -2.092
HETATM    8 C     2    2     1.575  -1.165   0.864
HETATM    9 O     2    2     1.610  -1.407  -0.560
HETATM   10 H     2    2     2.442  -1.670   1.309
HETATM   11 C     2    2     0.324  -1.793   1.493
HETATM   12 H     2    2     0.028  -2.630   0.853
HETATM   13 C     2    2     2.712  -0.670  -1.094
HETATM   14 O     2    2     3.883  -1.432  -1.113
HETATM   15 H     2    2     2.420  -0.370  -2.103
HETATM   16 C     2    2     2.998   0.480  -0.085
HETATM   17 O     2    2     4.230   0.131   0.507
HETATM   18 H     2    2     3.026   1.471  -0.552
HETATM   19 C     2    2    -2.108  -1.676   1.974
HETATM   20 H     2    2    -1.880  -2.470   2.695
HETATM   21 H     2    2    -2.776  -0.956   2.458
HETATM   22 C     2    2    -2.758  -2.231   0.738
HETATM   23 C     2    2    -3.206  -1.299  -0.238
HETATM   24 C     2    2    -3.862  -1.789  -1.386
HETATM   25 C     2    2    -4.066  -3.159  -1.555
HETATM   26 C     2    2    -3.614  -4.071  -0.598
HETATM   27 C     2    2    -2.960  -3.598   0.543
HETATM   28 O     2    2    -3.013   0.009  -0.061
HETATM   29 H     2    2    -4.226  -1.072  -2.118
HETATM   30 H     2    2    -4.581  -3.516  -2.443
HETATM   31 H     2    2    -3.767  -5.137  -0.737
HETATM   32 C     2    2    -2.596   2.977  -0.459
HETATM   33 C     2    2    -2.724   4.350  -0.635
HETATM   34 C     2    2    -1.637   5.169  -0.332
HETATM   35 C     2    2    -0.460   4.592   0.142
HETATM   36 C     2    2    -0.412   3.210   0.303
HETATM   37 H     2    2    -3.396   2.277  -0.676
HETATM   38 H     2    2    -3.655   4.763  -1.008
HETATM   39 H     2    2    -1.700   6.245  -0.466
HETATM   40 H     2    2     0.405   5.202   0.384
HETATM   41 C     2    2     0.806   2.521   0.876
HETATM   42 H     2    2     1.722   2.956   0.463
HETATM   43 H     2    2     0.837   2.641   1.969
HETATM   44 C     2    2     1.880   0.340   0.965
HETATM   45 H     2    2     2.209   0.646   1.964
HETATM   46 H     2    2    -0.667  -0.309   2.463
HETATM   47 C     2    2     4.926  -0.754  -0.386
HETATM   48 C     2    2     5.700  -1.767   0.437
HETATM   49 H     2    2     6.200  -2.481  -0.224
HETATM   50 H     2    2     6.457  -1.258   1.041
HETATM   51 H     2    2     5.024  -2.312   1.100
HETATM   52 C     2    2     5.801   0.039  -1.355
HETATM   53 H     2    2     6.274  -0.637  -2.073
HETATM   54 H     2    2     5.205   0.768  -1.913
HETATM   55 H     2    2     6.581   0.575  -0.806
HETATM   56 H     2    2     0.596  -2.214   2.469
HETATM   57 H     2    2    -2.615  -4.300   1.299
```

$Cu^{II}L4$ HF-DFT (B3LYP)/6-31G*/PCM optimized structure

ZPE corrected energy = -3034.298108 hartree

pentacoordinate distorted square pyramidal structure

(pdb format)

```
HEADER
HETATM    1  C    2    2       5.677  -0.840  -1.353
HETATM    2  C    2    2       4.713  -1.442  -0.333
HETATM    3  C    2    2       5.354  -2.490   0.558
HETATM    4  H    2    2       4.617  -2.894   1.257
HETATM    5  H    2    2       6.177  -2.046   1.126
HETATM    6  H    2    2       5.750  -3.307  -0.051
HETATM    7  H    2    2       6.051  -1.620  -2.023
HETATM    8  H    2    2       6.525  -0.375  -0.843
HETATM    9  H    2    2       5.178  -0.078  -1.961
HETATM   10  O    2    2       3.584  -2.025  -1.012
HETATM   11  O    2    2       4.148  -0.414   0.497
HETATM   12  C    2    2       2.967   0.052  -0.119
HETATM   13  H    2    2       3.123   0.997  -0.653
HETATM   14  C    2    2       2.525  -1.114  -1.049
HETATM   15  H    2    2       2.271  -0.846  -2.077
HETATM   16  C    2    2       1.850   0.131   0.941
HETATM   17  H    2    2       2.234   0.447   1.917
HETATM   18  O    2    2       0.807   1.028   0.507
HETATM   19  C    2    2       1.091   2.426   0.663
HETATM   20  H    2    2       1.269   2.647   1.726
HETATM   21  H    2    2       1.996   2.702   0.106
HETATM   22  C    2    2      -0.115   3.147   0.138
HETATM   23  N    2    2      -0.244   4.478  -0.071
HETATM   24  C    2    2       0.755   5.512   0.195
HETATM   25  H    2    2       0.503   6.400  -0.386
HETATM   26  H    2    2       1.744   5.165  -0.116
HETATM   27  C    2    2      -1.534   4.691  -0.529
HETATM   28  H    2    2      -1.890   5.682  -0.770
HETATM   29  C    2    2      -2.137   3.465  -0.586
HETATM   30  H    2    2      -3.135   3.195  -0.895
HETATM   31  N    2    2      -1.239   2.512  -0.165
HETATM   32 CU    2    2      -1.263   0.545   0.033
HETATM   33  C    2    2       1.342  -1.322   0.934
HETATM   34  H    2    2       2.132  -1.912   1.416
HETATM   35  O    2    2       1.338  -1.659  -0.470
HETATM   36  H    2    2      -0.094  -1.185  -1.548
HETATM   37  O    2    2      -0.745  -0.500  -1.803
HETATM   38  H    2    2      -1.538  -0.964  -2.124
HETATM   39  C    2    2       0.021  -1.735   1.594
HETATM   40  H    2    2      -0.355  -2.599   1.039
HETATM   41  H    2    2       0.234  -2.075   2.616
HETATM   42  N    2    2      -1.056  -0.715   1.632
HETATM   43  C    2    2      -2.391  -1.315   1.987
HETATM   44  C    2    2      -3.077  -1.904   0.788
HETATM   45  C    2    2      -3.415  -1.015  -0.271
HETATM   46  O    2    2      -3.099   0.278  -0.194
HETATM   47  C    2    2      -4.100  -1.531  -1.390
HETATM   48  C    2    2      -4.438  -2.883  -1.454
HETATM   49  C    2    2      -4.094  -3.754  -0.416
HETATM   50  C    2    2      -3.413  -3.255   0.698
HETATM   51  H    2    2      -3.152  -3.924   1.515
HETATM   52  H    2    2      -4.351  -4.807  -0.473
HETATM   53  H    2    2      -4.972  -3.260  -2.322
HETATM   54  H    2    2      -4.379  -0.844  -2.185
HETATM   55  H    2    2      -2.263  -2.062   2.780
HETATM   56  H    2    2      -2.984  -0.487   2.389
HETATM   57  H    2    2      -0.821  -0.065   2.384
HETATM   58  H    2    2       0.774   5.771   1.258
```