# Electronic Supplementary Information

## DFT Calculations:

## Typical ORCA Input File for **2a**:

```
# ORCA calculation on py3TACCu3Cl3 cosmo infinity
! RKS BP86 RI TZVP TZV/J TightSCF Opt
# ----------------------------------------

%method SpecialGridAtoms =29
       SpecialGridIntAcc=7
       end

%basis NewGTO 29 "Wachters" end
      NewAuxGTO 29 "TZV/J" end
      end

%rel method ZORA
    ModelDens rhoZORA
    velit 137.0359895
    end

%cosmo epsilon 99999.9
      refrac 1.33
      end

* xyz 0 1
Cu    0.820251    8.739687    2.995973
Cu   -1.479320    7.943703    4.316961
Cu   -0.852807   10.411467    4.339730
Cl   -0.427983    6.841377    2.514266
Cl   -2.899670    9.585902    3.402835
Cl    0.412914   11.017381    2.510951
N     0.592076    9.911909    6.101606
N    -1.539479   11.665328    5.750232
N    -0.102020    7.614718    6.075980
N    -2.796412    7.074153    5.599891
N     1.891621    8.286720    4.896646
N     2.744408    8.773724    2.263611
C    -0.785994   11.816292    6.872080
C    -2.769206   12.235325    5.713843
C     1.947040    9.524480    5.693862
C    -0.019122    8.837032    6.893002
C     0.596035   11.195230    6.825872
C     3.699699    8.571739    3.206817
C     3.111895    9.321963    1.081442
C     3.240830    7.862255    4.465280
C     1.246202    7.206467    5.658054
C    -0.765515    6.516878    6.811047
C    -2.274131    6.649560    6.780293
C    -4.143337    7.155062    5.480847
H    -0.401420    6.429050    7.859865
H    -0.491809    5.570352    6.296501
H     1.154827    6.323597    4.996539
H     1.865456    6.930218    6.553165
H     0.582697    8.640962    7.822196
H    -1.039188    9.139982    7.197577
H     2.378733   10.332255    5.071344
H     2.603910    9.375624    6.593382
H     1.269937   11.880367    6.266912
H     1.009984   11.103454    7.856585
H     3.182233    6.776379    4.236752
H     3.996158    7.977420    5.275903
C    -3.082605    6.304637    7.874298
C    -5.017819    6.807499    6.518308
H    -4.513701    7.536598    4.516401
H    -2.617569    5.979840    8.817122
C    -4.479332    6.375362    7.742063
H    -6.104785    6.882661    6.365107
H    -5.134436    6.105068    8.583726
C    -3.286207   12.988845    6.774923
H    -3.350807   12.050467    4.796719
C    -2.508766   13.147524    7.934833
H    -4.287399   13.435520    6.691113
C    -1.242908   12.541198    7.983818
H    -2.885199   13.724091    8.793038
H    -0.606572   12.627840    8.877363
C     4.432856    9.687158    0.790021
H     2.306111    9.475702    0.346328
C     5.418122    9.496194    1.772475
H     4.678562   10.119527   -0.190847
C     5.041033    8.932949    3.002836
H     6.463204    9.786465    1.587357
H     5.779764    8.768107    3.801852
*

%eprnmr  ori IGLO
        LocMet FB
        Nuclei = all C {shift}
        Nuclei = all H {shift}
        end
```

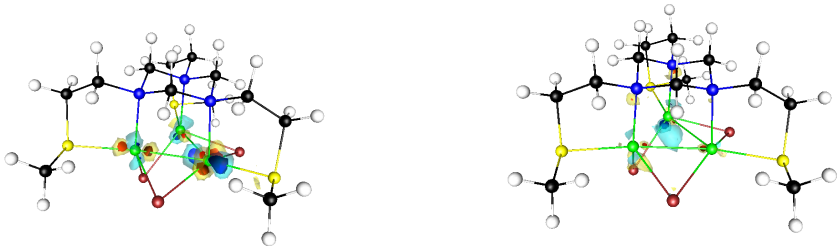

**Fig. S1** Contour plot of the HOMO (-3.69eV, HOMO-1 at -3.76eV) and the LUMO of **3*** (-1.25eV).

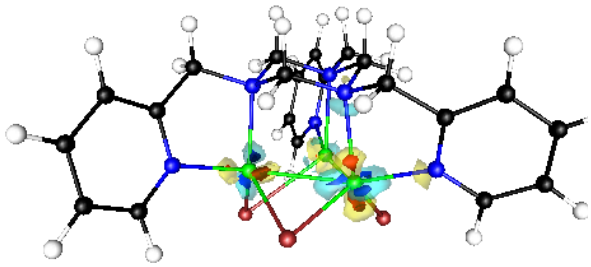

**Fig. S2** Contour plot of the HOMO of sym **2a** (-3.56eV)

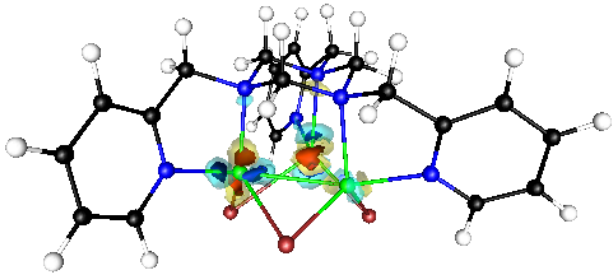

**Fig. S3** Contour plot of the HOMO-1 of **2a** (-3.69eV)

**Table S1:** Average calculated bond lengths in Å to copper

| Compound | Method[a] | Cu-Cu | Cu-X | Cu-N(TAC) | Cu-N(py)/S |
|---|---|---|---|---|---|
| **2a** - asym | | 2.63 | 2.38 | 2.22 | 2.05 |
| | VDW | 2.62 | 2.36 | 2.21 | 2.03 |
| **2a** – sym[b] | VDW | 2.57 | 2.41 | 2.18 | 2.04 |
| | | | | | |
| **3a** - asym | | 2.59 | 2.49 | 2.21 | 2.05 |
| | VDW | 2.56 | 2.49 | 2.20 | 2.05 |
| | | | | | |
| **2*** - asym | | 2.65 | 2.37 | 2.17 | 2.39 |
| | VDW | 2.62 | 2.35 | 2.15 | 2.36 |
| **2*** - Cl-sym[d] | | 2.67 | 2.36 | 2.16 | 2.40 |
| | | | | | |
| **3*** - asym | | 2.64 | 2.49 | 2.17 | 2.41 |
| | VDW | 2.61 | 2.48 | 2.16 | 2.36 |
| **3*** - sym[c] | VDW | 2.59 | 2.49 | 2.15 | 2.35 |
| **3*** - Br-sym[e] | | 2.66 | 2.47 | 2.16 | 2.42 |
| | | | | | |
| | | | | | |
| **4*** - asym | | 2.57 | 2.52 | 2.20 | 2.45 |
| | VDW | 2.57 | 2.54 | 2.15 | 2.38 |

[a]Method shown in the typical Input file unless stated as follows: VDW: with Grimme's van der Waals correction; XRAY: all non-hydrogen atoms fixed at the position of the X-ray structure
[b]1.76 KJ/mol above **2a** – asym
[c]4.87 KJ/mol above **4*** – asym
[d]0.72 KJ/mol above **2*** – asym
[e]0.03 KJ/mol above **3*** – asym

xyz files for all optimised structures mentioned above containing the coordinates are given as separate ESI files.

**Table S2:** Calculated average NMR shifts for **2a**, **3a**, **2*** and **3*** in ppm relative to TMS at the same computational method.

$^{1}$H:

| Compound | Method | $H_{eq}$ | $H_{ax}$ | $NCH_2$ | 3-py | 4-py | 5-py | 6-py | $CH_2S$ | Me |
|---|---|---|---|---|---|---|---|---|---|---|
| **2a** - asym | | 3.84 | 3.34 | 3.89 | 7.44 | 8.21 | 7.61 | 8.64 | | |
| | VDW | 3.70 | 3.20 | 3.77 | 7.40 | 8.13 | 7.53 | 8.67 | | |
| **2a** - sym | VDW | 3.67 | 3.20 | 3.77 | 7.57 | 8.30 | 7.77 | 8.87 | | |
| | exp | 3.6 | 3.3 | 3.9 | 7.4 | 7.8 | 7.3 | 8.5 | | |
| | | | | | | | | | | |
| **3a** -asym | | 3.94 | 3.37 | 3.97 | 7.47 | 8.24 | 7.64 | 8.81 | | |
| | VDW | 3.87 | 3.20 | 3.85 | 7.37 | 8.17 | 7.53 | 8.77 | | |
| | XRAY | 4.07 | 3.20 | 3.84 | 7.30 | 8.03 | 7.40 | 8.53 | | |
| | B3LYP | 4.20 | 3.43 | 4.03 | 7.54 | 8.37 | 7.50 | 8.97 | | |
| | exp | 3.7-4.3 | 3.2 | 3.9 | 7.3 | 7.7 | 7.2 | 8.7 | | |
| | | | | | | | | | | |
| **2*** - asym | | 4.04 | 3.04 | 2.87 | | | | | 2.89 | 2.06 |
| | VDW | 4.03 | 2.93 | 2.87 | | | | | 2.82 | 2.13 |
| **2*** - Cl-sym | | 3.87 | 3.14 | 2.94 | | | | | 2.82 | 2.04 |
| | exp | 4.1 | 2.7 | 2.6 | | | | | 2.6 | |
| | | | | | | | | | | |
| **3*** - asym | | 4.11 | 3.07 | 2.89 | | | | | 2.89 | 2.08 |
| | VDW | 4.30 | 2.93 | 2.88 | | | | | 2.87 | 2.17 |
| **3*** - sym | VDW | 4.30 | 2.93 | 2.87 | | | | | 2.97 | 2.21 |
| **3*** - Br-sym | | 3.94 | 3.14 | 2.94 | | | | | 2.82 | 2.05 |
| | exp | 4.2 | 2.8 | 2.6 | | | | | 2.6 | |

$^{13}$C:

| Compound | Method | $C_{ring}$ | $NCH_2$ | 2-py | 3-py | 4-py | 5-py | 6-py | $CH_2S$ | Me |
|---|---|---|---|---|---|---|---|---|---|---|
| **2a** - asym | | 79.9 | 61.6 | 156.1 | 126.7 | 136.3 | 128.0 | 149.0 | | |
| | VDW | 78.3 | 61.5 | 155.8 | 127.1 | 136.0 | 127.9 | 149.3 | | |
| **2a** - sym | VDW | 79.2 | 61.5 | 155.9 | 126.9 | 137.0 | 128.1 | 149.4 | | |
| | exp | 74 | 58 | 156 | 125 | 139 | 125 | 150 | | |
| | | | | | | | | | | |
| **3a** -asym | | 79.7 | 61.6 | 156.1 | 126.3 | 137.0 | 127.7 | 149.4 | | |
| | VDW | 77.7 | 61.1 | 155.5 | 126.7 | 136.6 | 127.5 | 149.6 | | |
| | XRAY | 80.6 | 63.1 | 153.5 | 124.1 | 133.7 | 124.0 | 147.6 | | |
| | B3LYP | 80.7 | 63.6 | 161.6 | 128.2 | 141.8 | 127.5 | 155.4 | | |
| | exp | 75 | 58 | 155 | 124 | 138 | 124 | 150 | | |
| | | | | | | | | | | |
| **2*** - asym | | 81.1 | 53.2 | | | | | | 40.9 | 21.4 |
| | VDW | 81.3 | 51.7 | | | | | | 40.9 | 22.0 |
| **2*** - Cl-sym | | 82.6 | 53.6 | | | | | | 40.7 | 21.1 |
| | exp | 74 | 53 | | | | | | 30 | |
| | | | | | | | | | | |
| **3*** - asym | | 81.2 | 53.5 | | | | | | 40.4 | 21.3 |
| | VDW | 80.5 | 51.8 | | | | | | 40.9 | 23.0 |
| **3*** - sym | VDW | 79.7 | 53.1 | | | | | | 41.2 | 25.5 |
| **3*** - Br-sym | | 82.4 | 53.7 | | | | | | 40.3 | 20.8 |
| | exp | 74 | 53 | | | | | | 30 | |

[a]Method shown in the typical Input file unless stated as follows: VDW: with Grimme's van der Waals correction; XRAY: all non-hydrogen atoms fixed at the position of the X-ray structure; B3LYP: single point B3LYP calculation at the H optimised X ray structure positions; exp: typical experimental value.

## Plots for Molecular Structures from X-ray Crystallography not included in the main text

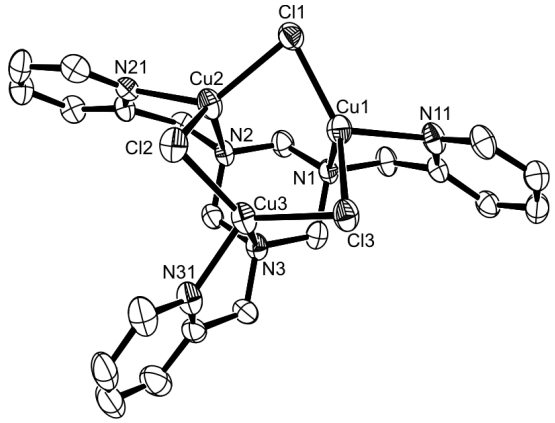


**Fig. S4** Thermal ellipsoid (50%) plot of the *asym* conformer in **2a**. Hydrogen atoms omitted for clarity.

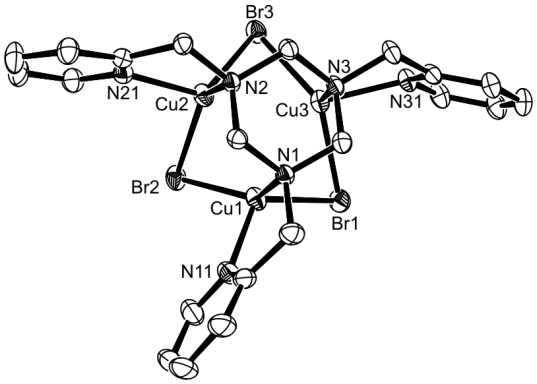


**Fig. S5** Thermal ellipsoid (50%) plot of the *asym* conformer found for **3a** (**3a-B**) Hydrogen atoms omitted for clarity.

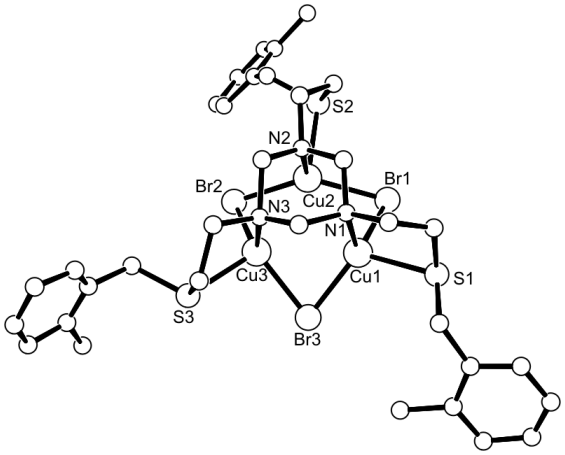


**Fig. S6** Ball and stick plot of **3h**. Hydrogen atoms omitted for clarity.