Density Functional Calculations Reveal a Flexible Version of the Copper Paddlewheel Unit: Implications for Metal Organic Frameworks

K. A. H. Alzahrania and R. J. Deeth†
Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK.
† Current address: School of Chemistry, University of Edinburgh, Edinburgh, EH9 3FJ, UK

Electronic Supporting Information

Computational details

Most calculations used ORCA version 3.0.3.[1] A typical geometry optimisation/frequency calculation employed the Becke-Perdew functional, def2-SVP basis sets, a COSMO solvation field with water as the solvent and, for the NHC systems, the Grimme D3 dispersion corrections. For copper species, a spin-unrestricted formalism was employed with a total spin $S = 1$.

```
UKS BP RI def2-SVP def2-SVP/J Grid6 NoFinalGrid TightSCF SlowConv Cosmo(water) NumFreq
!KDIIS
!D3BJ
```

Magnetic coupling constants employed the broken-symmetry (BS) scheme implemented in ORCA (FlipSpin) and used the B3LYP functional with def2-TZVP basis sets and the COSMO(water) solvation field. BS geometry optimisations included Grimme's D3 correction.

The structural studies were based on the spin triplet potential energy surface rather than the BS surface for two reasons.

Firstly, we found no significant geometry change between the structure optimised on the (ferromagnetic) triplet state and the BS solution. The effect on the magnetic coupling was noticeable but does not change our conclusions. For the symmetric TBP NHC system, $[Cu_2(acetate)_4(Me_2NHC)_2]$, the computed J value for the $S = 1$ geometry is -139.55 cm^{-1} and for the BS geometry, J = -166.35 cm^{-1}.

Secondly, while geometry optimisations were possible on the BS surface, numerical frequency calculations (necessary since we were using a COSMO field) were unstable. We thus opted to use the triplet surface throughout.

The high-symmetry (constrained) optimisations used the Amsterdam Density Functional (ADF) 2014 code[2-4] since, in our hands, we find it more convenient than ORCA when specifying particular electronic configurations. Geometry optimisations employed the Becke-Perdew functional with DZP basis sets on all atoms apart from the metals for which TZP bases were employed. Small frozen cores were selected and a COSMO(water) correction, as implemented in ADF, was used. Given the qualitative nature of the high-symmetry study, we did not bother with any dispersion corrections nor were vibrational frequencies computed.

1. F. Neese, U. Becker, D. Ganiouchine, S. Koßmann, T. Petrenko, C. Riplinger and F. Wennmohs, Max Planck Institute for Chemnical Energy Conversion, Muellheim, ORCA 3.0.1 edn., 2014.
2. G. T. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. F. Guerra, S. J. A. Van Gisbergen, J. G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, 22, 931-967.
3. C. Fonseca Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, *Theor. Chem. Acc.*, 1998, 99, 391.
4. E. J. Baerends, T. Ziegler, J. Autschbach, D. Bashford, A. Bérces, F. M. Bickelhaupt, C. Bo, P. M. Boerrigter, L. Cavallo, D. P. Chong, L. Deng, R. M. Dickson, D. E. Ellis, M. van Faassen, L. Fan, T. H. Fischer, C. Fonseca Guerra, A. Ghysels, A. Giammona, S. J. A. van Gisbergen, A. W. Götz, J. A. Groeneveld, O. V. Gritsenko, M. Grüning, S. Gusarov, F. E. Harris, P. van den Hoek, C. R. Jacob, H. Jacobsen, L. Jensen, J. W. Kaminski, G. van Kessel, F. Kootstra, A. Kovalenko, M. V. Krykunov, E. van Lenthe, D. A. McCormack, A. Michalak, M. Mitoraj, J. Neugebauer, V. P. Nicu, L. Noodleman, V. P. Osinga, S. Patchkovskii, P. H. T. Philipsen, D. Post, C. C. Pye, W. Ravenek, J. I. Rodríguez, P. Ros, P. R. T. Schipper, G. Schreckenbach, J. S. Seldenthuis, M. Seth, J. G. Snijders, M. Solà, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T. A. Wesolowski, E. M. van Wezenbeek, G. Wiesenekker, S. K. Wolff, T. K. Woo and A. L. Yakovlev, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, Netherlands, 2014.
5. A. M. Magill, K. J. Cavell and B. F. Yates, *J. Am. Chem. Soc.*, 2004, 126, 8717-8724.
6. K. D. Vogiatzis, W. Klopper, A. Mavrandonakis and K. Fink, *Chemphyschem*, 2011, 12, 3307-3319.

Cartesian coordinates, energies and lowest 12 vibrational frequencies to confirm local minimum achieved (where computed)

Complexes are listed in the order in which they appear in the manuscript. Nomenclature: $[Cu_2(O_2CR)_4L_n]$ → CuPR.nL

The electronic energy is included in parentheses after the name of the appropriate computer code and is a total electronic energy for ORCA and a binding energy for ADF.

The necessary MO occupations to generate the desired energy state in ADF are included. If no occupation specified, that geometry corresponds to the automatically located Aufbau state.

CuPH.2NH3: 'elongated': ORCA (-4150.49254046 Eh)

Cu	-0.005099000	0.000448000	1.333207000
O	1.428995000	-1.432605000	1.143311000
O	-1.437377000	1.433604000	1.136557000
O	-1.437409000	-1.432899000	1.136845000
O	1.428860000	1.433661000	1.142840000
C	1.824657000	-1.824503000	0.005025000
C	-1.824692000	-1.824725000	-0.004415000
Cu	0.004855000	-0.000205000	-1.333202000
O	-1.429092000	1.432959000	-1.143223000
O	1.437207000	-1.433393000	-1.136411000

O	1.437112000	1.433051000	-1.136973000
O	-1.429218000	-1.433338000	-1.142925000
C	-1.824659000	1.824857000	-0.004894000
C	1.824302000	1.824970000	0.004288000
H	-2.618582000	-2.618218000	-0.007027000
H	-2.618060000	2.618827000	-0.007916000
H	2.617823000	2.618832000	0.006838000
H	2.618221000	-2.618302000	0.008049000
N	-0.002564000	-0.001223000	-3.511452000
H	0.938875000	-0.027108000	-3.928611000
H	-0.502895000	-0.808032000	-3.911396000
H	-0.458704000	0.830474000	-3.913239000
N	0.002372000	0.000300000	3.511455000
H	-0.939083000	-0.024187000	3.928665000
H	0.501719000	-0.806913000	3.911813000
H	0.459563000	0.831647000	3.912774000

0:	0.00 cm**-1
1:	0.00 cm**-1
2:	0.00 cm**-1
3:	0.00 cm**-1
4:	0.00 cm**-1
5:	0.00 cm**-1
6:	33.46 cm**-1
7:	49.39 cm**-1
8:	60.80 cm**-1
9:	70.58 cm**-1
10:	77.27 cm**-1
11:	84.80 cm**-1
12:	89.56 cm**-1

CuPH.2NH3: 'mixed': ORCA (-4150.48497904 Eh)

Cu	-0.007629000	0.000505000	1.263830000
O	1.461325000	-1.468174000	1.142750000
O	-1.475998000	1.469546000	1.133177000
O	-1.476126000	-1.468539000	1.133442000
O	1.461353000	1.469495000	1.142442000
C	1.860290000	-1.860146000	0.007301000
C	-1.860515000	-1.860372000	-0.006812000
Cu	0.007343000	0.000023000	-1.263803000
O	-1.461288000	1.469057000	-1.142753000
O	1.475966000	-1.468734000	-1.133089000
O	1.475721000	1.469116000	-1.133488000
O	-1.461724000	-1.468736000	-1.142414000
C	-1.860043000	1.861135000	-0.007265000
C	1.859961000	1.861134000	0.006765000
H	-2.654933000	-2.655089000	-0.011970000
H	-2.654208000	2.656105000	-0.012771000
H	2.654160000	2.656071000	0.011823000
H	2.654830000	-2.654735000	0.012791000
N	-0.004030000	-0.001473000	-3.332069000
H	0.944262000	-0.029843000	-3.731978000
H	-0.514195000	-0.815776000	-3.702314000
H	-0.466483000	0.839236000	-3.705886000
N	0.003768000	-0.000090000	3.332077000
H	-0.944544000	-0.027217000	3.732024000
H	0.513070000	-0.814727000	3.702768000
H	0.467130000	0.840337000	3.705406000

0:	0.00	cm**-1
1:	0.00	cm**-1
2:	0.00	cm**-1
3:	0.00	cm**-1
4:	0.00	cm**-1
5:	0.00	cm**-1
6:	8.79	cm**-1
7:	12.51	cm**-1
8:	84.42	cm**-1
9:	86.70	cm**-1
10:	87.12	cm**-1
11:	89.28	cm**-1
12:	91.19	cm**-1

CuPH.2H2O: $T_0(D_{2h})$: ADF (-5.10539471 a.u.)

Cu	0.000000000	0.000000000	-1.275396000
Cu	0.000000000	0.000000000	1.275396000
O	1.426069000	1.421853000	-1.140404000
O	1.426069000	-1.421853000	-1.140404000
O	-1.426069000	1.421853000	-1.140404000
O	-1.426069000	-1.421853000	-1.140404000
C	1.821355000	1.815160000	0.000000000
C	1.821355000	-1.815160000	0.000000000
O	1.426069000	1.421853000	1.140404000
O	-1.426069000	-1.421853000	1.140404000
C	-1.821355000	-1.815160000	0.000000000
O	1.426069000	-1.421853000	1.140404000
O	-1.426069000	1.421853000	1.140404000
C	-1.821355000	1.815160000	0.000000000
O	0.000000000	0.000000000	-3.548713000
H	0.783560000	0.000000000	-4.141379000
H	-0.783560000	0.000000000	-4.141379000
O	0.000000000	0.000000000	3.548713000
H	0.783560000	0.000000000	4.141379000
H	-0.783560000	0.000000000	4.141379000
H	-2.602677000	2.595139000	0.000000000
H	-2.602677000	-2.595139000	0.000000000
H	2.602677000	-2.595139000	0.000000000
H	2.602677000	2.595139000	0.000000000

CuPH.2H2O: $T_M(D_{2h})$: ADF (-5.07922654 a.u.)

Cu	0.000000000	0.000000000	-1.227489000
Cu	0.000000000	0.000000000	1.227489000
O	1.467907000	1.463810000	-1.136654000
O	1.467907000	-1.463810000	-1.136654000
O	-1.467907000	1.463810000	-1.136654000
O	-1.467907000	-1.463810000	-1.136654000
C	1.863957000	1.859658000	0.000000000
C	1.863957000	-1.859658000	0.000000000
O	1.467907000	1.463810000	1.136654000
O	-1.467907000	-1.463810000	1.136654000
C	-1.863957000	-1.859658000	0.000000000
O	1.467907000	-1.463810000	1.136654000
O	-1.467907000	1.463810000	1.136654000
C	-1.863957000	1.859658000	0.000000000
O	0.000000000	0.000000000	-3.316186000
H	0.793920000	0.000000000	-3.894232000
H	-0.793920000	0.000000000	-3.894232000
O	0.000000000	0.000000000	3.316186000
H	0.793920000	0.000000000	3.894232000

H	-0.793920000	0.000000000	3.894232000
H	-2.644802000	2.641828000	0.000000000
H	-2.644802000	-2.641828000	0.000000000
H	2.644802000	-2.641828000	0.000000000
H	2.644802000	2.641828000	0.000000000

CuPCH3.2H2O: $T_0(D_2)$: ADF (-7.51870373 a.u.)

Cu	0.000000000	0.000000000	1.260700000
Cu	0.000000000	0.000000000	-1.260700000
O	1.421500000	-1.427700000	1.114200000
O	1.427400000	1.411100000	1.158400000
O	-1.427400000	-1.411100000	1.158400000
O	-1.421500000	1.427700000	1.114200000
C	1.837100000	-1.829800000	-0.023600000
C	1.837100000	1.829800000	0.023600000
O	1.427400000	-1.411100000	-1.158400000
O	-1.427400000	1.411100000	-1.158400000
C	-1.837100000	1.829800000	-0.023600000
O	1.421500000	1.427700000	-1.114200000
O	-1.421500000	-1.427700000	-1.114200000
C	-1.837100000	-1.829800000	0.023600000
O	0.000000000	0.000000000	3.566200000
H	0.780500000	0.051300000	4.160500000
H	-0.780500000	-0.051300000	4.160500000
O	0.000000000	0.000000000	-3.566200000
H	0.780500000	-0.051300000	-4.160500000
H	-0.780500000	0.051300000	-4.160500000
C	-2.905900000	2.893200000	-0.019000000
H	-2.528700000	3.782700000	0.504900000
H	-3.199200000	3.161700000	-1.039700000
H	-3.781300000	2.525900000	0.534900000
C	2.905900000	2.893200000	0.019000000
H	2.528700000	3.782700000	-0.504900000
H	3.199200000	3.161700000	1.039700000
H	3.781300000	2.525900000	-0.534900000
C	2.905900000	-2.893200000	-0.019000000
H	3.199200000	-3.161700000	-1.039700000
H	3.781300000	-2.525900000	0.534900000
H	2.528700000	-3.782700000	0.504900000
C	-2.905900000	-2.893200000	0.019000000
H	-3.199200000	-3.161700000	1.039700000
H	-3.781300000	-2.525900000	-0.534900000
H	-2.528700000	-3.782700000	-0.504900000

CuPCH3.2H2O: $T_M(D_2)$: ADF (-7.48941290 a.u.)

Cu	0.000000000	0.000000000	-1.215677000
Cu	0.000000000	0.000000000	1.215677000
O	-1.481625000	1.457362000	-1.089093000
O	1.434060000	1.479642000	-1.174149000
O	-1.434060000	-1.479642000	-1.174149000
O	1.481625000	-1.457362000	-1.089093000
C	-1.870641000	1.883397000	0.046860000
C	1.870641000	1.883397000	-0.046860000
O	-1.434060000	1.479642000	1.174149000
O	1.434060000	-1.479642000	1.174149000
C	1.870641000	-1.883397000	0.046860000
O	1.481625000	1.457362000	1.089093000
O	-1.481625000	-1.457362000	1.089093000
C	-1.870641000	-1.883397000	-0.046860000
O	0.000000000	0.000000000	-3.323139000
H	0.258406000	0.749214000	-3.902544000

H	-0.258406000	-0.749214000	-3.902544000
O	0.000000000	0.000000000	3.323139000
H	-0.258406000	0.749214000	3.902544000
H	0.258406000	-0.749214000	3.902544000
C	2.937418000	-2.953322000	0.048672000
H	3.828996000	-2.577179000	-0.472533000
H	3.203094000	-3.246280000	1.070325000
H	2.572242000	-3.829425000	-0.505396000
C	2.937418000	2.953322000	-0.048672000
H	3.828996000	2.577179000	0.472533000
H	3.203094000	3.246280000	-1.070325000
H	2.572242000	3.829425000	0.505396000
C	-2.937418000	2.953322000	0.048672000
H	-3.203094000	3.246280000	1.070325000
H	-2.572242000	3.829425000	-0.505396000
H	-3.828996000	2.577179000	-0.472533000
C	-2.937418000	-2.953322000	-0.048672000
H	-3.203094000	-3.246280000	-1.070325000
H	-2.572242000	-3.829425000	0.505396000
H	-3.828996000	-2.577179000	0.472533000

CuPCH3.2NH3: $T_0(C_{2h})$: ADF (-7.92078556 a.u.)

Cu	-1.299400000	0.000900000	0.000000000
O	-1.135100000	1.426500000	1.431000000
O	-1.137000000	-1.433100000	-1.427000000
O	-1.137000000	-1.433100000	1.427000000
O	-1.135100000	1.426500000	-1.431000000
C	0.000600000	1.843200000	1.835500000
C	-0.000600000	-1.843200000	1.835500000
Cu	1.299400000	-0.000900000	0.000000000
O	1.135100000	-1.426500000	-1.431000000
O	1.137000000	1.433100000	1.427000000
O	1.137000000	1.433100000	-1.427000000
O	1.135100000	-1.426500000	1.431000000
C	-0.000600000	-1.843200000	-1.835500000
C	0.000600000	1.843200000	-1.835500000
C	-0.002900000	2.944000000	2.869200000
H	0.911300000	2.913900000	3.473900000
H	-0.039200000	3.911700000	2.345400000
H	-0.889200000	2.870100000	3.511000000
C	0.002900000	-2.944000000	2.869200000
H	0.889200000	-2.870100000	3.511000000
H	-0.911300000	-2.913900000	3.473900000
H	0.039200000	-3.911700000	2.345400000
C	0.002900000	-2.944000000	-2.869200000
H	-0.911300000	-2.913900000	-3.473900000
H	0.889200000	-2.870100000	-3.511000000
H	0.039200000	-3.911700000	-2.345400000
C	-0.002900000	2.944000000	-2.869200000
H	-0.889200000	2.870100000	-3.511000000
H	-0.039200000	3.911700000	-2.345400000
H	0.911300000	2.913900000	-3.473900000
N	3.530100000	-0.007200000	0.000000000
H	3.932400000	0.937700000	0.000000000
H	3.917600000	-0.486600000	0.821600000
H	3.917600000	-0.486600000	-0.821600000
N	-3.530100000	0.007200000	0.000000000
H	-3.917600000	0.486600000	-0.821600000
H	-3.932400000	-0.937700000	0.000000000
H	-3.917600000	0.486600000	0.821600000

CuPCH3.2NH3: $T_M(C_{2h})$: ADF (-7.91005747 a.u.)
symmetry C(2h)
occupations
A.g 21.0 // 21.0
B.g 16.0 // 15.0
A.u 16.0 // 16.0
B.u 21.0 // 20.0
end

Cu	-1.249700000	-0.001100000	0.000000000
O	-1.141500000	1.472100000	1.469300000
O	-1.126300000	-1.469100000	-1.473200000
O	-1.126300000	-1.469100000	1.473200000
O	-1.141500000	1.472100000	-1.469300000
C	-0.007700000	1.881300000	1.880700000
C	0.007700000	-1.881300000	1.880700000
Cu	1.249700000	0.001100000	0.000000000
O	1.141500000	-1.472100000	-1.469300000
O	1.126300000	1.469100000	1.473200000
O	1.126300000	1.469100000	-1.473200000
O	1.141500000	-1.472100000	1.469300000
C	0.007700000	-1.881300000	-1.880700000
C	-0.007700000	1.881300000	-1.880700000
C	-0.006000000	2.977000000	2.926300000
H	0.876800000	2.895700000	3.572000000
H	0.035500000	3.947800000	2.409000000
H	-0.922600000	2.945500000	3.527300000
C	0.006000000	-2.977000000	2.926300000
H	0.922600000	-2.945500000	3.527300000
H	-0.876800000	-2.895700000	3.572000000
H	-0.035500000	-3.947800000	2.409000000
C	0.006000000	-2.977000000	-2.926300000
H	-0.876800000	-2.895700000	-3.572000000
H	0.922600000	-2.945500000	-3.527300000
H	-0.035500000	-3.947800000	-2.409000000
C	-0.006000000	2.977000000	-2.926300000
H	-0.922600000	2.945500000	-3.527300000
H	0.035500000	3.947800000	-2.409000000
H	0.876800000	2.895700000	-3.572000000
N	3.328300000	-0.020800000	0.000000000
H	3.728200000	0.925200000	0.000000000
H	3.692200000	-0.508800000	0.827600000
H	3.692200000	-0.508800000	-0.827600000
N	-3.328300000	0.020800000	0.000000000
H	-3.692200000	0.508800000	-0.827600000
H	-3.728200000	-0.925200000	0.000000000
H	-3.692200000	0.508800000	0.827600000

CuPCH3.2py: $T_0(D_2)$: ADF (-11.62463259 a.u.)

Cu	1.290700000	0.000000000	0.000000000
Cu	-1.290700000	0.000000000	0.000000000
O	1.121000000	-1.438200000	-1.428600000
O	1.152000000	1.403400000	-1.446600000
O	1.152000000	-1.403400000	1.446600000
O	1.121000000	1.438200000	1.428600000
C	-0.018000000	-1.819100000	-1.856900000
C	0.018000000	1.819100000	-1.856900000
O	-1.152000000	-1.403400000	-1.446600000
O	-1.152000000	1.403400000	1.446600000

```
C       -0.018000000      1.819100000      1.856900000
O       -1.121000000      1.438200000     -1.428600000
O       -1.121000000     -1.438200000      1.428600000
C        0.018000000     -1.819100000      1.856900000
C       -0.016000000      2.861300000      2.950700000
H        0.495500000      3.765600000      2.591600000
H       -1.036400000      3.113500000      3.259800000
H        0.549500000      2.481200000      3.813400000
C        0.016000000      2.861300000     -2.950700000
H       -0.495500000      3.765600000     -2.591600000
H        1.036400000      3.113500000     -3.259800000
H       -0.549500000      2.481200000     -3.813400000
C       -0.016000000     -2.861300000     -2.950700000
H       -1.036400000     -3.113500000     -3.259800000
H        0.549500000     -2.481200000     -3.813400000
H        0.495500000     -3.765600000     -2.591600000
C        0.016000000     -2.861300000      2.950700000
H        1.036400000     -3.113500000      3.259800000
H       -0.549500000     -2.481200000      3.813400000
H       -0.495500000     -3.765600000      2.591600000
N        3.518700000      0.000000000      0.000000000
C        4.209800000     -0.143700000      1.146200000
C        4.209800000      0.143700000     -1.146200000
C        5.602000000     -0.151200000      1.190800000
C        5.602000000      0.151200000     -1.190800000
C        6.312200000      0.000000000      0.000000000
H        3.615200000     -0.261600000      2.053600000
H        3.615200000      0.261600000     -2.053600000
H        6.116200000     -0.273400000      2.145100000
H        6.116200000      0.273400000     -2.145100000
H        7.403700000      0.000000000      0.000000000
N       -3.518700000      0.000000000      0.000000000
C       -4.209800000     -0.143700000     -1.146200000
C       -4.209800000      0.143700000      1.146200000
C       -5.602000000     -0.151200000     -1.190800000
C       -5.602000000      0.151200000      1.190800000
C       -6.312200000      0.000000000      0.000000000
H       -3.615200000     -0.261600000     -2.053600000
H       -3.615200000      0.261600000      2.053600000
H       -6.116200000     -0.273400000     -2.145100000
H       -6.116200000      0.273400000      2.145100000
H       -7.403700000      0.000000000      0.000000000
```

CuPCH3.2py: $T_M(D_2)$: ADF (-11.61336618 a.u.)

```
symmetry D(2)
occupations
A   24.0  1.0  //  24.0  1.0
B1  23.0       //  23.0
B2  23.0       //  23.0
B3  23.0  1.0 1.0 // 23.0 0.0 0.0
end
Cu       1.244300000      0.000000000      0.000000000
Cu      -1.244300000      0.000000000      0.000000000
O        1.136100000     -1.546600000     -1.399300000
O        1.121700000      1.387500000     -1.537900000
O        1.121700000     -1.387500000      1.537900000
O        1.136100000      1.546600000      1.399300000
C        0.003800000     -1.878500000     -1.876600000
C       -0.003800000      1.878500000     -1.876600000
O       -1.121700000     -1.387500000     -1.537900000
```

O	-1.121700000	1.387500000	1.537900000
C	0.003800000	1.878500000	1.876600000
O	-1.136100000	1.546600000	-1.399300000
O	-1.136100000	-1.546600000	1.399300000
C	-0.003800000	-1.878500000	1.876600000
C	0.004800000	2.958200000	2.939400000
H	0.439000000	3.877100000	2.520000000
H	-1.009200000	3.163200000	3.300000000
H	0.641600000	2.643900000	3.778300000
C	-0.004800000	2.958200000	-2.939400000
H	-0.439000000	3.877100000	-2.520000000
H	1.009200000	3.163200000	-3.300000000
H	-0.641600000	2.643900000	-3.778300000
C	0.004800000	-2.958200000	-2.939400000
H	-1.009200000	-3.163200000	-3.300000000
H	0.641600000	-2.643900000	-3.778300000
H	0.439000000	-3.877100000	-2.520000000
C	-0.004800000	-2.958200000	2.939400000
H	1.009200000	-3.163200000	3.300000000
H	-0.641600000	-2.643900000	3.778300000
H	-0.439000000	-3.877100000	2.520000000
N	3.318500000	0.000000000	0.000000000
C	3.997000000	-0.082100000	1.157900000
C	3.997000000	0.082100000	-1.157900000
C	5.387800000	-0.083100000	1.198000000
C	5.387800000	0.083100000	-1.198000000
C	6.096000000	0.000000000	0.000000000
H	3.395700000	-0.152600000	2.064600000
H	3.395700000	0.152600000	-2.064600000
H	5.900600000	-0.149500000	2.158000000
H	5.900600000	0.149500000	-2.158000000
H	7.187300000	0.000000000	0.000000000
N	-3.318500000	0.000000000	0.000000000
C	-3.997000000	-0.082100000	-1.157900000
C	-3.997000000	0.082100000	1.157900000
C	-5.387800000	-0.083100000	-1.198000000
C	-5.387800000	0.083100000	1.198000000
C	-6.096000000	0.000000000	0.000000000
H	-3.395700000	-0.152600000	-2.064600000
H	-3.395700000	0.152600000	2.064600000
H	-5.900600000	-0.149500000	-2.158000000
H	-5.900600000	0.149500000	2.158000000
H	-7.187300000	0.000000000	0.000000000

CuPCH3.2CN: $T_0(D_2)$: ADF (-7.95330195)

Cu	0.000000000	-1.369530000	0.000000000
Cu	0.000000000	1.369530000	0.000000000
O	-1.430383000	-1.110928000	1.465270000
O	-1.460366000	-1.162540000	-1.419503000
O	1.460366000	-1.162540000	1.419503000
O	1.430383000	-1.110928000	-1.465270000
C	-1.855029000	0.027527000	1.846892000
C	-1.855029000	-0.027527000	-1.846892000
O	-1.460366000	1.162540000	1.419503000
O	1.460366000	1.162540000	-1.419503000
C	1.855029000	0.027527000	-1.846892000
O	-1.430383000	1.110928000	-1.465270000
O	1.430383000	1.110928000	1.465270000
C	1.855029000	-0.027527000	1.846892000
C	2.931186000	0.025695000	-2.910668000

```
H        2.554020000     -0.485613000     -3.807790000
H        3.235522000      1.046275000     -3.168848000
H        3.801418000     -0.538773000     -2.546805000
C       -2.931186000     -0.025695000     -2.910668000
H       -2.554020000      0.485613000     -3.807790000
H       -3.235522000     -1.046275000     -3.168848000
H       -3.801418000      0.538773000     -2.546805000
C       -2.931186000      0.025695000      2.910668000
H       -3.235522000      1.046275000      3.168848000
H       -3.801418000     -0.538773000      2.546805000
H       -2.554020000     -0.485613000      3.807790000
C        2.931186000     -0.025695000      2.910668000
H        3.235522000     -1.046275000      3.168848000
H        3.801418000      0.538773000      2.546805000
H        2.554020000      0.485613000      3.807790000
C        0.000000000     -3.498369000      0.000000000
N        0.000000000     -4.675022000      0.000000000
C        0.000000000      3.498369000      0.000000000
N        0.000000000      4.675022000      0.000000000
```

CuPCH3.2CN: $T_M(D_2)$: ADF (-7.94619279)

```
symmetry D(2)
occupations
A   20.0  //  20.0
B1  18.0  //  18.0
B2  20.0  //  18.0
B3  18.0  //  18.0
end
Cu       0.000000000     -1.306914000      0.000000000
Cu       0.000000000      1.306914000      0.000000000
O       -1.414693000     -1.128942000      1.554538000
O       -1.547925000     -1.131972000     -1.405339000
O        1.547925000     -1.131972000      1.405339000
O        1.414693000     -1.128942000     -1.554538000
C       -1.887674000      0.004214000      1.887457000
C       -1.887674000     -0.004214000     -1.887457000
O       -1.547925000      1.131972000      1.405339000
O        1.547925000      1.131972000     -1.405339000
C        1.887674000      0.004214000     -1.887457000
O       -1.414693000      1.128942000     -1.554538000
O        1.414693000      1.128942000      1.554538000
C        1.887674000     -0.004214000      1.887457000
C        2.960031000     -0.000191000     -2.960918000
H        2.565935000     -0.482111000     -3.866844000
H        3.290394000      1.017121000     -3.198415000
H        3.817429000     -0.595346000     -2.615456000
C       -2.960031000      0.000191000     -2.960918000
H       -2.565935000      0.482111000     -3.866844000
H       -3.290394000     -1.017121000     -3.198415000
H       -3.817429000      0.595346000     -2.615456000
C       -2.960031000     -0.000191000      2.960918000
H       -3.290394000      1.017121000      3.198415000
H       -3.817429000     -0.595346000      2.615456000
H       -2.565935000     -0.482111000      3.866844000
C        2.960031000      0.000191000      2.960918000
H        3.290394000     -1.017121000      3.198415000
H        3.817429000      0.595346000      2.615456000
H        2.565935000      0.482111000      3.866844000
C        0.000000000     -3.333568000      0.000000000
N        0.000000000     -4.508519000      0.000000000
```

C	0.000000000	3.333568000	0.000000000
N	0.000000000	4.508519000	0.000000000

CuPCH3.2NHC: $T_0(C_{2v})$: ADF (-12.97521013 a.u.)
symmetry C(2v)
occupations
A1 36.0 // 36.0
A2 18.0 // 16.0
B1 25.0 // 25.0
B2 25.0 // 25.0
end

Cu	0.000000000	0.000000000	1.384800000
O	-1.446100000	-1.432000000	1.135200000
O	1.446100000	1.432000000	1.135200000
O	-1.446100000	1.432000000	1.135200000
O	1.446100000	-1.432000000	1.135200000
C	-1.844800000	-1.845200000	-0.000700000
C	-1.844800000	1.845200000	-0.000700000
Cu	0.000000000	0.000000000	-1.385600000
O	1.436100000	1.444800000	-1.137900000
O	-1.436100000	-1.444800000	-1.137900000
O	1.436100000	-1.444800000	-1.137900000
O	-1.436100000	1.444800000	-1.137900000
C	1.844800000	1.845200000	-0.000700000
C	1.844800000	-1.845200000	-0.000700000
C	-2.888000000	-2.942700000	0.002000000
H	-3.505900000	-2.894300000	-0.903000000
H	-2.371900000	-3.915200000	0.014300000
H	-3.517800000	-2.878200000	0.897800000
C	-2.888000000	2.942700000	0.002000000
H	-3.505900000	2.894300000	-0.903000000
H	-3.517800000	2.878200000	0.897800000
H	-2.371900000	3.915200000	0.014300000
C	2.888000000	2.942700000	0.002000000
H	3.517800000	2.878200000	0.897800000
H	3.505900000	2.894300000	-0.903000000
H	2.371900000	3.915200000	0.014300000
C	2.888000000	-2.942700000	0.002000000
H	3.517800000	-2.878200000	0.897800000
H	2.371900000	-3.915200000	0.014300000
H	3.505900000	-2.894300000	-0.903000000
C	0.000000000	0.000000000	-3.573300000
N	-1.070100000	0.000000000	-4.424400000
N	1.070100000	0.000000000	-4.424400000
C	0.680500000	0.000000000	-5.754700000
C	-0.680500000	0.000000000	-5.754700000
H	-1.391000000	0.000000000	-6.573000000
H	1.391000000	0.000000000	-6.573000000
C	0.000000000	0.000000000	3.574400000
N	0.000000000	-1.070300000	4.425600000
N	0.000000000	1.070300000	4.425600000
C	0.000000000	0.680700000	5.756000000
C	0.000000000	-0.680700000	5.756000000
H	0.000000000	-1.391600000	6.574200000
H	0.000000000	1.391600000	6.574200000
C	0.000000000	2.467400000	3.998700000
H	0.000000000	2.489900000	2.905300000
H	-0.896800000	2.972600000	4.381700000
H	0.896800000	2.972600000	4.381700000
C	0.000000000	-2.467400000	3.998700000

H	-0.896800000	-2.972600000	4.381700000
H	0.000000000	-2.489900000	2.905300000
H	0.896800000	-2.972600000	4.381700000
C	2.466900000	0.000000000	-3.997100000
H	2.488500000	0.000000000	-2.903900000
H	2.972500000	-0.896500000	-4.380000000
H	2.972500000	0.896500000	-4.380000000
C	-2.466900000	0.000000000	-3.997100000
H	-2.488500000	0.000000000	-2.903900000
H	-2.972500000	0.896500000	-4.380000000
H	-2.972500000	-0.896500000	-4.380000000

CuPCH3.2NHC: $T_M(C_{2v})$: ADF (-12.97515986)
symmetry C(2v)
occupations
A1 36.0 // 35.0
A2 18.0 // 17.0
B1 25.0 // 25.0
B2 25.0 // 25.0
end

Cu	0.000000000	0.000000000	1.338100000
O	-1.495000000	-1.454300000	1.136200000
O	1.495000000	1.454300000	1.136200000
O	-1.495000000	1.454300000	1.136200000
O	1.495000000	-1.454300000	1.136200000
C	-1.885700000	-1.876600000	0.002700000
C	-1.885700000	1.876600000	0.002700000
Cu	0.000000000	0.000000000	-1.342800000
O	1.463300000	1.493000000	-1.133400000
O	-1.463300000	-1.493000000	-1.133400000
O	1.463300000	-1.493000000	-1.133400000
O	-1.463300000	1.493000000	-1.133400000
C	1.885700000	1.876600000	0.002700000
C	1.885700000	-1.876600000	0.002700000
C	-2.940600000	-2.969100000	0.007900000
H	-3.552100000	-2.926000000	-0.901700000
H	-2.431700000	-3.945200000	0.032700000
H	-3.576800000	-2.893800000	0.898200000
C	-2.940600000	2.969100000	0.007900000
H	-3.552100000	2.926000000	-0.901700000
H	-3.576800000	2.893800000	0.898200000
H	-2.431700000	3.945200000	0.032700000
C	2.940600000	2.969100000	0.007900000
H	3.576800000	2.893800000	0.898200000
H	3.552100000	2.926000000	-0.901700000
H	2.431700000	3.945200000	0.032700000
C	2.940600000	-2.969100000	0.007900000
H	3.576800000	-2.893800000	0.898200000
H	2.431700000	-3.945200000	0.032700000
H	3.552100000	-2.926000000	-0.901700000
C	0.000000000	0.000000000	-3.413300000
N	-1.075000000	0.000000000	-4.251200000
N	1.075000000	0.000000000	-4.251200000
C	0.680300000	0.000000000	-5.578500000
C	-0.680300000	0.000000000	-5.578500000
H	-1.391500000	0.000000000	-6.395800000
H	1.391500000	0.000000000	-6.395800000
C	0.000000000	0.000000000	3.409200000
N	0.000000000	-1.075100000	4.246100000
N	0.000000000	1.075100000	4.246100000

C	0.000000000	0.680500000	5.573800000
C	0.000000000	-0.680500000	5.573800000
H	0.000000000	-1.392600000	6.390500000
H	0.000000000	1.392600000	6.390500000
C	0.000000000	2.476200000	3.827600000
H	0.000000000	2.510800000	2.735700000
H	-0.897100000	2.973800000	4.218500000
H	0.897100000	2.973800000	4.218500000
C	0.000000000	-2.476200000	3.827600000
H	-0.897100000	-2.973800000	4.218500000
H	0.000000000	-2.510800000	2.735700000
H	0.897100000	-2.973800000	4.218500000
C	2.476200000	0.000000000	-3.834100000
H	2.511700000	0.000000000	-2.742400000
H	2.973500000	-0.897100000	-4.225700000
H	2.973500000	0.897100000	-4.225700000
C	-2.476200000	0.000000000	-3.834100000
H	-2.511700000	0.000000000	-2.742400000
H	-2.973500000	0.897100000	-4.225700000
H	-2.973500000	-0.897100000	-4.225700000

CuPCF3.2NHC: $T_0(C_{2v})$: ADF (-13.10982211 a.u.)

```
symmetry C(2v)
occupations
A1   45.0  // 45.0
A2   27.0  // 25.0
B1   34.0  // 34.0
B2   34.0  // 34.0
end
```

Cu	0.000000000	0.000000000	1.468200000
O	-1.437400000	-1.432800000	1.129400000
O	1.437400000	1.432800000	1.129400000
O	-1.437400000	1.432800000	1.129400000
O	1.437400000	-1.432800000	1.129400000
C	-1.803100000	-1.808500000	-0.015200000
C	-1.803100000	1.808500000	-0.015200000
Cu	0.000000000	0.000000000	-1.501700000
O	1.435700000	1.438500000	-1.159100000
O	-1.435700000	-1.438500000	-1.159100000
O	1.435700000	-1.438500000	-1.159100000
O	-1.435700000	1.438500000	-1.159100000
C	1.803100000	1.808500000	-0.015200000
C	1.803100000	-1.808500000	-0.015200000
C	-2.871000000	-2.943000000	0.013300000
C	-2.871000000	2.943000000	0.013300000
C	2.871000000	2.943000000	0.013300000
C	2.871000000	-2.943000000	0.013300000
C	0.000000000	0.000000000	-3.636700000
N	-1.071600000	0.000000000	-4.483600000
N	1.071600000	0.000000000	-4.483600000
C	0.680400000	0.000000000	-5.811300000
C	-0.680400000	0.000000000	-5.811300000
H	-1.392100000	0.000000000	-6.628300000
H	1.392100000	0.000000000	-6.628300000
C	0.000000000	0.000000000	3.598900000
N	0.000000000	-1.071500000	4.445500000
N	0.000000000	1.071500000	4.445500000
C	0.000000000	0.680400000	5.773500000
C	0.000000000	-0.680400000	5.773500000
H	0.000000000	-1.392800000	6.590000000

H	0.000000000	1.392800000	6.590000000
C	0.000000000	2.471500000	4.028900000
H	0.000000000	2.511200000	2.937000000
H	-0.897000000	2.972000000	4.416000000
H	0.897000000	2.972000000	4.416000000
C	0.000000000	-2.471500000	4.028900000
H	-0.897000000	-2.972000000	4.416000000
H	0.000000000	-2.511200000	2.937000000
H	0.897000000	-2.972000000	4.416000000
C	2.471900000	0.000000000	-4.067600000
H	2.513100000	0.000000000	-2.975900000
H	2.972200000	-0.896800000	-4.455400000
H	2.972200000	0.896800000	-4.455400000
C	-2.471900000	0.000000000	-4.067600000
H	-2.513100000	0.000000000	-2.975900000
H	-2.972200000	0.896800000	-4.455400000
H	-2.972200000	-0.896800000	-4.455400000
F	3.461100000	-3.121800000	-1.189500000
F	3.838900000	-2.672900000	0.927600000
F	2.276500000	-4.117100000	0.373400000
F	-3.461100000	-3.121800000	-1.189500000
F	-2.276500000	-4.117100000	0.373400000
F	-3.838900000	-2.672900000	0.927600000
F	-3.838900000	2.672900000	0.927600000
F	-3.461100000	3.121800000	-1.189500000
F	-2.276500000	4.117100000	0.373400000
F	3.838900000	2.672900000	0.927600000
F	2.276500000	4.117100000	0.373400000
F	3.461100000	3.121800000	-1.189500000

CuPCF3.2NHC: $T_M(C_{2v})$: ADF (-13.11965195 a.u.)

```
symmetry C(2v)
occupations
A1   45.0  // 44.0
A2   27.0  // 26.0
B1   34.0  // 34.0
B2   34.0  // 34.0
end
```

Cu	0.000000000	0.000000000	1.403900000
O	-1.488700000	-1.442900000	1.136300000
O	1.488700000	1.442900000	1.136300000
O	-1.488700000	1.442900000	1.136300000
O	1.488700000	-1.442900000	1.136300000
C	-1.856800000	-1.820500000	-0.005600000
C	-1.856800000	1.820500000	-0.005600000
Cu	0.000000000	0.000000000	-1.442400000
O	1.468900000	1.475600000	-1.148300000
O	-1.468900000	-1.475600000	-1.148300000
O	1.468900000	-1.475600000	-1.148300000
O	-1.468900000	1.475600000	-1.148300000
C	1.856800000	1.820500000	-0.005600000
C	1.856800000	-1.820500000	-0.005600000
C	-2.954000000	-2.925800000	0.019600000
C	-2.954000000	2.925800000	0.019600000
C	2.954000000	2.925800000	0.019600000
C	2.954000000	-2.925800000	0.019600000
C	0.000000000	0.000000000	-3.492700000
N	-1.076700000	0.000000000	-4.323400000
N	1.076700000	0.000000000	-4.323400000
C	0.680000000	0.000000000	-5.649400000

C	-0.680000000	0.000000000	-5.649400000
H	-1.392300000	0.000000000	-6.465500000
H	1.392300000	0.000000000	-6.465500000
C	0.000000000	0.000000000	3.454400000
N	0.000000000	-1.077200000	4.283300000
N	0.000000000	1.077200000	4.283300000
C	0.000000000	0.680300000	5.609600000
C	0.000000000	-0.680300000	5.609600000
H	0.000000000	-1.393500000	6.425000000
H	0.000000000	1.393500000	6.425000000
C	0.000000000	2.479900000	3.869400000
H	0.000000000	2.525700000	2.778600000
H	-0.897600000	2.974300000	4.261100000
H	0.897600000	2.974300000	4.261100000
C	0.000000000	-2.479900000	3.869400000
H	-0.897600000	-2.974300000	4.261100000
H	0.000000000	-2.525700000	2.778600000
H	0.897600000	-2.974300000	4.261100000
C	2.480100000	0.000000000	-3.912400000
H	2.529200000	0.000000000	-2.821800000
H	2.973700000	-0.897300000	-4.306200000
H	2.973700000	0.897300000	-4.306200000
C	-2.480100000	0.000000000	-3.912400000
H	-2.529200000	0.000000000	-2.821800000
H	-2.973700000	0.897300000	-4.306200000
H	-2.973700000	-0.897300000	-4.306200000
F	3.624100000	-3.012300000	-1.153800000
F	3.860900000	-2.699400000	1.005300000
F	2.370800000	-4.137800000	0.262100000
F	-3.624100000	-3.012300000	-1.153800000
F	-2.370800000	-4.137800000	0.262100000
F	-3.860900000	-2.699400000	1.005300000
F	-3.860900000	2.699400000	1.005300000
F	-2.370800000	4.137800000	0.262100000
F	-3.624100000	3.012300000	-1.153800000
F	3.860900000	2.699400000	1.005300000
F	2.370800000	4.137800000	0.262100000
F	3.624100000	3.012300000	-1.153800000

CuPCH3.2NHC: Symmetric TBP T_M: ORCA (-4803.96162140 Eh)

Cu	1.097364000	0.372482000	-0.447739000
O	-0.314327000	0.277554000	-2.051761000
O	1.204952000	-0.066626000	1.641484000
O	0.469115000	2.234959000	-0.036221000
O	1.706743000	-1.494323000	-0.869962000
C	-1.494596000	-0.133918000	-2.230816000
C	-0.716042000	2.352087000	0.431902000
Cu	-1.529168000	-0.736241000	0.533971000
O	-0.776154000	-0.866960000	2.391762000
O	-2.268629000	-0.609130000	-1.329261000
O	-0.250900000	-2.330545000	-0.095300000
O	-1.503726000	1.402045000	0.700160000
C	0.433601000	-0.481231000	2.551414000
C	0.967063000	-0.502465000	3.978025000
H	2.011451000	-0.870188000	3.987238000
H	0.977766000	0.537143000	4.367099000
H	0.335742000	-1.123424000	4.639856000
C	0.907004000	-2.451479000	-0.585910000
C	4.633820000	1.619539000	-2.427968000
H	5.233800000	1.632974000	-3.343596000

N	3.400212000	0.978692000	-2.348831000
C	2.860680000	1.105180000	-1.103822000
N	3.770398000	1.835012000	-0.398922000
C	4.867673000	2.166722000	-1.189316000
H	5.710457000	2.754620000	-0.811667000
C	-4.901071000	-2.767224000	2.110567000
H	-5.305351000	-3.655742000	2.606152000
N	-3.550785000	-2.630592000	1.799625000
C	-3.305398000	-1.435468000	1.192254000
N	-4.519553000	-0.820641000	1.123158000
C	-4.732388000	0.487910000	0.509516000
H	-5.424198000	1.082648000	1.135664000
H	-5.163768000	0.374364000	-0.504284000
H	-3.754341000	0.998488000	0.437970000
C	-5.517370000	-1.617786000	1.677843000
H	-6.566325000	-1.306928000	1.717934000
C	3.583287000	2.236968000	0.992982000
H	3.276658000	3.299725000	1.051056000
H	2.791993000	1.601749000	1.432193000
H	4.529909000	2.099941000	1.549407000
C	2.766657000	0.235253000	-3.435082000
H	1.697350000	0.104353000	-3.186121000
H	2.867896000	0.801611000	-4.380272000
H	3.241412000	-0.758532000	-3.552606000
C	-2.513446000	-3.612919000	2.103781000
H	-2.880059000	-4.627894000	1.859295000
H	-2.242354000	-3.571297000	3.176869000
H	-1.624291000	-3.376074000	1.491236000
C	1.432548000	-3.860217000	-0.831843000
H	1.848631000	-4.253484000	0.119543000
H	2.237319000	-3.863003000	-1.590306000
H	0.607950000	-4.530321000	-1.141038000
C	-1.218250000	3.773760000	0.649774000
H	-1.789192000	3.834359000	1.596514000
H	-1.914201000	4.033318000	-0.175218000
H	-0.387154000	4.502767000	0.655813000
C	-2.051435000	-0.095793000	-3.648207000
H	-3.150662000	-0.212892000	-3.657427000
H	-1.761576000	0.851201000	-4.143502000
H	-1.598556000	-0.925954000	-4.229548000

0:	0.00	cm**-1
1:	0.00	cm**-1
2:	0.00	cm**-1
3:	0.00	cm**-1
4:	0.00	cm**-1
5:	0.00	cm**-1
6:	14.50	cm**-1
7:	17.54	cm**-1
8:	26.27	cm**-1
9:	29.53	cm**-1
10:	33.90	cm**-1
11:	37.89	cm**-1
12:	41.18	cm**-1

CuPCH3.2NHC: Asymmetric TBP T_M: ORCA (-4803.96120825 Eh)

Cu	-0.178189000	0.272126000	1.539137000
O	-1.668064000	-1.070840000	1.484093000
O	1.285877000	1.654157000	1.521618000
O	-1.459746000	1.628229000	0.646325000

O	1.319054000	-1.251364000	0.834838000
C	-1.969410000	-1.530737000	0.325968000
C	-1.727714000	2.028258000	-0.523671000
Cu	0.146613000	0.118597000	-1.514469000
O	1.598072000	1.426836000	-0.711913000
O	-1.405461000	-1.227078000	-0.760105000
O	1.462004000	-1.388387000	-1.419099000
O	-1.176737000	1.627334000	-1.603419000
C	1.868412000	1.928189000	0.415379000
C	1.759281000	-1.763157000	-0.227956000
C	-3.136051000	-2.510287000	0.275392000
C	-2.837467000	3.059487000	-0.680556000
C	2.961081000	2.988205000	0.482101000
C	2.702927000	-2.956266000	-0.120768000
C	0.069358000	-0.063356000	-3.521466000
N	-1.014048000	-0.306956000	-4.311090000
N	1.116477000	0.049797000	-4.386917000
C	0.699749000	-0.121577000	-5.704219000
C	-0.655177000	-0.345201000	-5.655839000
H	-1.382156000	-0.525576000	-6.454330000
H	1.389871000	-0.071133000	-6.552540000
C	0.047106000	-0.041698000	3.522887000
N	0.157311000	-1.227102000	4.187885000
N	0.013302000	0.905584000	4.504957000
C	0.094052000	0.326317000	5.767292000
C	0.187027000	-1.029608000	5.565149000
H	0.284200000	-1.857010000	6.275424000
H	0.088996000	0.918422000	6.688331000
C	-0.146401000	2.335289000	4.245155000
H	0.384558000	2.578197000	3.306995000
H	-1.219322000	2.593980000	4.143748000
H	0.285914000	2.909438000	5.084761000
C	0.207705000	-2.533700000	3.533985000
H	0.865155000	-3.205891000	4.117067000
H	-0.807729000	-2.971175000	3.468385000
H	0.612427000	-2.388249000	2.515094000
C	2.492820000	0.296258000	-3.966096000
H	2.944688000	1.077540000	-4.606320000
H	2.474422000	0.634628000	-2.914604000
H	3.094423000	-0.630606000	-4.040114000
C	-2.375296000	-0.454480000	-3.800491000
H	-2.314327000	-0.760996000	-2.739689000
H	-2.920859000	0.506544000	-3.874077000
H	-2.907243000	-1.224773000	-4.389798000
H	3.248446000	-3.134578000	-1.065856000
H	3.416840000	-2.802780000	0.711649000
H	2.102788000	-3.859487000	0.117379000
H	-4.026341000	-1.983102000	-0.126879000
H	-2.899888000	-3.339614000	-0.419324000
H	-3.381691000	-2.907720000	1.277299000
H	-2.881444000	3.724003000	0.202843000
H	-2.701000000	3.651002000	-1.605201000
H	-3.807120000	2.523508000	-0.754974000
H	3.396819000	3.050070000	1.496530000
H	2.512956000	3.974390000	0.237974000
H	3.750633000	2.782059000	-0.265284000

0:	0.00 cm**-1
1:	0.00 cm**-1
2:	0.00 cm**-1
3:	0.00 cm**-1

4:	0.00	cm**-1
5:	0.00	cm**-1
6:	11.05	cm**-1
7:	18.03	cm**-1
8:	28.85	cm**-1
9:	31.88	cm**-1
10:	35.20	cm**-1
11:	37.31	cm**-1
12:	41.49	cm**-1

AZOGOL: $[Zn_2(O_2CCH_2Ph)_4(NMes_2NHC)_2]$: ORCA (-7242.98610438 Eh)

Zn	3.938230000	16.615161000	5.676933000
N	1.028353000	15.904828000	4.848262000
O	4.625792000	15.106677000	4.425428000
O	4.312647000	17.968203000	4.092885000
C	1.868587000	16.678899000	5.602709000
C	-0.310579000	16.236398000	5.066144000
H	-1.129829000	15.724946000	4.551414000
C	1.409431000	14.860375000	3.922968000
C	1.508281000	13.533802000	4.398200000
C	1.759721000	12.519586000	3.451553000
H	1.828028000	11.476378000	3.802046000
C	1.923426000	12.799477000	2.080010000
C	1.854493000	14.144922000	1.660310000
H	1.994283000	14.386411000	0.593123000
C	1.604860000	15.196405000	2.563502000
C	5.713114000	14.510884000	4.169228000
C	1.383866000	13.220684000	5.868435000
H	2.225616000	13.675971000	6.434519000
H	1.404130000	12.128842000	6.046451000
H	0.446266000	13.626792000	6.302700000
C	2.204502000	11.695205000	1.085852000
H	3.286466000	11.655286000	0.833523000
H	1.659347000	11.853783000	0.133558000
H	1.922138000	10.701658000	1.486483000
C	1.577740000	16.634670000	2.107008000
H	2.412028000	17.200737000	2.576577000
H	0.636856000	17.146864000	2.399594000
H	1.678174000	16.703989000	1.006274000
H	5.955728000	12.391074000	3.950290000
H	4.536651000	13.069735000	3.082250000
C	6.427003000	13.273525000	2.037490000
C	5.897390000	13.867094000	0.868820000
H	4.879201000	14.287273000	0.896804000
C	6.648402000	13.925842000	-0.317757000
H	6.214118000	14.389109000	-1.218449000
C	7.949880000	13.392347000	-0.358876000
H	8.538417000	13.434416000	-1.289360000
C	8.491597000	12.803270000	0.798017000
H	9.509352000	12.382612000	0.778106000
H	8.166451000	12.284092000	2.884936000
C	5.607415000	13.228302000	3.309247000
C	7.736480000	12.747784000	1.983036000
O	6.874496000	14.844327000	4.559372000
Zn	7.151271000	16.547740000	5.786033000
O	6.563904000	17.706414000	4.176658000
C	5.495628000	18.161543000	3.673127000
O	4.611653000	18.055433000	7.007595000
C	5.701815000	18.559352000	7.410121000
O	6.871842000	18.234177000	7.042685000

O	6.375979000	15.423795000	7.359739000
C	5.259806000	14.995267000	7.777254000
O	4.118344000	15.227435000	7.273114000
C	-0.313069000	17.250528000	5.984620000
N	1.024323000	17.503409000	6.297127000
C	1.398593000	18.530427000	7.244756000
C	1.626819000	19.843277000	6.770589000
C	1.867487000	20.847954000	7.727410000
H	2.036441000	21.879872000	7.376915000
C	1.897227000	20.573339000	9.111334000
C	1.704060000	19.242395000	9.531430000
H	1.745095000	19.004373000	10.607604000
C	1.458611000	18.198383000	8.616152000
C	1.299981000	16.770653000	9.079098000
H	2.122948000	16.142836000	8.672123000
H	0.347513000	16.322378000	8.725861000
H	1.320847000	16.706710000	10.184466000
C	2.161281000	21.678759000	10.108926000
H	3.217512000	22.020148000	10.055009000
H	1.971328000	21.347336000	11.148870000
H	1.528888000	22.567901000	9.907813000
C	1.645327000	20.145225000	5.292728000
H	2.498353000	19.629554000	4.800018000
H	1.751227000	21.231227000	5.108926000
H	0.722036000	19.795571000	4.784621000
H	-1.134994000	17.812326000	6.439061000
C	5.301590000	14.135909000	9.064402000
H	6.363727000	13.913593000	9.278146000
H	4.919944000	14.786443000	9.880888000
C	4.483845000	12.865019000	9.000742000
C	3.137607000	12.831035000	9.425486000
H	2.676038000	13.750342000	9.818819000
C	2.385079000	11.645378000	9.357886000
H	1.338438000	11.641840000	9.700949000
C	2.966557000	10.466123000	8.857302000
H	2.379914000	9.534854000	8.806106000
C	4.305450000	10.485780000	8.425363000
H	4.771348000	9.567725000	8.032194000
C	5.053682000	11.673578000	8.497106000
H	6.102060000	11.683206000	8.157184000
C	9.221622000	16.487168000	5.862628000
N	10.111884000	17.186158000	5.092509000
C	11.432562000	16.880206000	5.427315000
C	11.372148000	15.961303000	6.439215000
N	10.016326000	15.736421000	6.687424000
C	9.579240000	14.815513000	7.713471000
C	9.427990000	13.448617000	7.382412000
C	9.123068000	12.554199000	8.426834000
H	9.015280000	11.482319000	8.189826000
C	8.960039000	12.987673000	9.760083000
C	9.083263000	14.364479000	10.033238000
H	8.939052000	14.724995000	11.065114000
C	9.386318000	15.302511000	9.025118000
C	9.469027000	16.778765000	9.326654000
H	8.664821000	17.326827000	8.788956000
H	10.432303000	17.218629000	8.993473000
H	9.361183000	16.968365000	10.412020000
C	8.634635000	11.997803000	10.856080000
H	7.606264000	11.594404000	10.734561000
H	8.693193000	12.463669000	11.859231000
H	9.321427000	11.126500000	10.835686000

C	9.555164000	12.975225000	5.955196000
H	8.745673000	13.417965000	5.333323000
H	9.484184000	11.871659000	5.895400000
H	10.519292000	13.284500000	5.499563000
H	12.160868000	15.452273000	7.001857000
H	12.285196000	17.340705000	4.918721000
C	9.796352000	18.135318000	4.046938000
C	9.692877000	19.504781000	4.381822000
C	9.506853000	20.420512000	3.326872000
H	9.439286000	21.495129000	3.566343000
C	9.413015000	20.004811000	1.982272000
C	9.484505000	18.624397000	1.704153000
H	9.394401000	18.277506000	0.661344000
C	9.668493000	17.665678000	2.720445000
C	9.693693000	16.189645000	2.411451000
H	8.823154000	15.681050000	2.878848000
H	10.605423000	15.695209000	2.808052000
H	9.648434000	16.008881000	1.320869000
C	9.200175000	21.012050000	0.874562000
H	8.121886000	21.260816000	0.767061000
H	9.545529000	20.623956000	-0.104111000
H	9.730791000	21.963602000	1.078777000
C	9.746766000	19.962763000	5.817706000
H	8.866426000	19.579654000	6.379309000
H	9.738573000	21.067546000	5.886279000
H	10.652216000	19.588771000	6.340665000
C	5.567453000	19.639050000	8.510766000
H	4.527055000	20.013199000	8.473179000
H	5.680937000	19.093953000	9.473275000
C	6.561016000	20.775044000	8.445346000
C	7.791677000	20.720398000	9.136222000
H	8.033999000	19.826075000	9.732690000
C	8.705956000	21.786977000	9.077806000
H	9.657890000	21.723210000	9.629265000
C	8.406334000	22.934325000	8.320814000
H	9.118593000	23.774151000	8.277509000
C	7.187319000	23.000815000	7.621468000
H	6.941805000	23.894997000	7.026271000
C	6.276778000	21.931787000	7.684810000
H	5.324429000	21.991560000	7.133723000
C	5.657540000	19.005483000	2.385791000
H	6.740943000	19.172352000	2.237495000
H	5.293759000	18.366612000	1.552428000
C	4.902104000	20.316104000	2.393140000
C	3.610390000	20.427648000	1.834041000
H	3.145840000	19.540092000	1.375940000
C	2.914641000	21.649495000	1.851002000
H	1.908954000	21.712244000	1.406096000
C	3.500430000	22.788332000	2.432841000
H	2.959007000	23.747900000	2.444289000
C	4.785322000	22.691221000	2.998240000
H	5.253847000	23.577544000	3.455438000
C	5.476541000	21.467644000	2.978191000
H	6.480575000	21.397372000	3.426282000

0:	0.00 cm**-1
1:	0.00 cm**-1
2:	0.00 cm**-1
3:	0.00 cm**-1
4:	0.00 cm**-1
5:	0.00 cm**-1

```
   6:       -10.03 cm**-1
   7:         5.17 cm**-1
   8:         9.29 cm**-1
   9:        10.07 cm**-1
  10:        12.16 cm**-1
  11:        13.29 cm**-1
  12:        15.03 cm**-1
```
The single negative value corresponds to a mesityl para-methyl group rotation which we do not consider significant.

AZOGOL[Cu}: [$Cu_2(O_2CCH_2Ph)_4(NMes_2NHC)_2$]: T_M ORCA (-6965.69749889)

Cu	-0.000000000	-0.000000000	1.582852000
N	-0.434481000	-0.986990000	4.402243000
O	-0.209735000	-1.928356000	0.682783000
O	-1.987559000	0.255216000	1.564842000
C	-0.000051000	-0.000045000	3.570130000
C	-0.275991000	-0.627774000	5.744029000
H	-0.562971000	-1.292734000	6.564086000
C	-0.995415000	-2.230465000	3.943259000
C	-0.127297000	-3.248419000	3.497641000
C	-0.713657000	-4.453083000	3.064024000
H	-0.051637000	-5.261249000	2.713006000
C	-2.109128000	-4.640134000	3.043579000
C	-2.935137000	-3.584594000	3.479479000
H	-4.029599000	-3.700085000	3.433439000
C	-2.401295000	-2.362267000	3.923398000
C	-0.444196000	-2.488874000	-0.415078000
C	1.359103000	-3.032098000	3.425117000
H	1.598723000	-2.310085000	2.616804000
H	1.889834000	-3.974679000	3.195409000
H	1.765550000	-2.605942000	4.365243000
C	-2.716328000	-5.903535000	2.485391000
H	-3.019815000	-5.739915000	1.427339000
H	-3.628128000	-6.201477000	3.041558000
H	-1.999431000	-6.748162000	2.501660000
C	-3.285642000	-1.192098000	4.270624000
H	-3.092091000	-0.369484000	3.547929000
H	-3.083179000	-0.795785000	5.286934000
H	-4.354669000	-1.473038000	4.214442000
H	-0.775961000	-4.467701000	-1.256872000
H	-0.814777000	-4.368419000	0.547798000
C	-2.616542000	-3.672319000	-0.444221000
C	-3.243674000	-2.735263000	0.405130000
H	-2.630789000	-2.158177000	1.109985000
C	-4.629304000	-2.528733000	0.340239000
H	-5.099108000	-1.789642000	1.007969000
C	-5.415481000	-3.255559000	-0.572107000
H	-6.503049000	-3.090075000	-0.626165000
C	-4.800545000	-4.194400000	-1.419147000
H	-5.404067000	-4.767044000	-2.141099000
H	-2.930742000	-5.122161000	-2.032403000
C	-1.111713000	-3.863684000	-0.392995000
C	-3.410667000	-4.396629000	-1.356018000
O	-0.255043000	-1.988835000	-1.581808000
Cu	0.000025000	-0.000000000	-1.600469000
O	-1.931886000	0.217192000	-0.701280000
C	-2.488072000	0.450018000	0.399133000
O	0.209711000	1.928322000	0.682810000
C	0.444196000	2.488862000	-0.415040000
O	0.255077000	1.988839000	-1.581780000

O	1.931915000	-0.217212000	-0.701241000
C	2.488084000	-0.450047000	0.399178000
O	1.987555000	-0.255258000	1.564880000
C	0.275574000	0.627712000	5.744046000
N	0.434261000	0.986921000	4.402278000
C	0.995239000	2.230399000	3.943352000
C	0.127159000	3.248375000	3.497702000
C	0.713554000	4.453038000	3.064133000
H	0.051571000	5.261220000	2.713085000
C	2.109029000	4.640065000	3.043763000
C	2.934999000	3.584507000	3.479691000
H	4.029465000	3.699984000	3.433706000
C	2.401125000	2.362177000	3.923565000
C	3.285429000	1.191980000	4.270814000
H	3.091948000	0.369407000	3.548054000
H	3.082855000	0.795606000	5.287076000
H	4.354463000	1.472924000	4.214755000
C	2.716265000	5.903468000	2.485625000
H	3.019773000	5.739871000	1.427576000
H	3.628053000	6.201380000	3.041826000
H	1.999386000	6.748110000	2.501901000
C	-1.359237000	3.032065000	3.425096000
H	-1.598809000	2.309967000	2.616849000
H	-1.889940000	3.974629000	3.195250000
H	-1.765743000	2.606031000	4.365252000
H	0.562276000	1.292705000	6.564174000
C	3.860027000	-1.124901000	0.384585000
H	4.362393000	-0.847507000	-0.563060000
H	4.469425000	-0.779519000	1.240953000
C	3.656057000	-2.626486000	0.460766000
C	4.350238000	-3.409620000	1.404417000
H	5.065005000	-2.925031000	2.088292000
C	4.129434000	-4.795052000	1.490753000
H	4.678132000	-5.390817000	2.236486000
C	3.202615000	-5.416596000	0.635960000
H	3.023718000	-6.500739000	0.709589000
C	2.505406000	-4.641646000	-0.309137000
H	1.776724000	-5.117017000	-0.985046000
C	2.730822000	-3.259991000	-0.397547000
H	2.176685000	-2.652703000	-1.126086000
C	0.000069000	0.000012000	-3.589406000
N	-0.996814000	0.411202000	-4.421762000
C	-0.633857000	0.261514000	-5.763644000
C	0.634104000	-0.261284000	-5.763620000
N	0.997005000	-0.411097000	-4.421733000
C	2.247859000	-0.953678000	-3.959861000
C	2.395584000	-2.358044000	-3.931733000
C	3.620533000	-2.875962000	-3.476207000
H	3.748905000	-3.968938000	-3.426452000
C	4.663816000	-2.035661000	-3.037479000
C	4.462796000	-0.642310000	-3.070260000
H	5.260891000	0.030631000	-2.716662000
C	3.255032000	-0.071686000	-3.516759000
C	3.025634000	1.414139000	-3.462230000
H	2.287259000	1.657280000	-2.669523000
H	2.614539000	1.806962000	-4.415161000
H	3.961058000	1.954060000	-3.223301000
C	5.929126000	-2.626714000	-2.466277000
H	5.749368000	-2.968641000	-1.422938000
H	6.754115000	-1.888058000	-2.439593000
H	6.265693000	-3.512425000	-3.042158000

C	1.239377000	-3.257378000	-4.287530000
H	0.408530000	-3.075662000	-3.571372000
H	1.533595000	-4.322751000	-4.230365000
H	0.848511000	-3.058745000	-5.306786000
H	1.305596000	-0.533666000	-6.583540000
H	-1.305297000	0.534113000	-6.583536000
C	-2.247665000	0.953796000	-3.959909000
C	-2.395395000	2.358160000	-3.931796000
C	-3.620339000	2.876094000	-3.476280000
H	-3.748727000	3.969068000	-3.426556000
C	-4.663624000	2.035801000	-3.037549000
C	-4.462602000	0.642454000	-3.070347000
H	-5.260721000	-0.030456000	-2.716761000
C	-3.254845000	0.071808000	-3.516829000
C	-3.025479000	-1.414026000	-3.462330000
H	-2.287007000	-1.657207000	-2.669724000
H	-2.614539000	-1.806867000	-4.415324000
H	-3.960898000	-1.953916000	-3.223306000
C	-5.928936000	2.626843000	-2.466347000
H	-5.749209000	2.968705000	-1.422978000
H	-6.753950000	1.888207000	-2.439733000
H	-6.265463000	3.512589000	-3.042195000
C	-1.239210000	3.257489000	-4.287637000
H	-0.408297000	3.075710000	-3.571578000
H	-1.533401000	4.322865000	-4.230396000
H	-0.848428000	3.058903000	-5.306931000
C	1.111715000	3.863670000	-0.392902000
H	0.776021000	4.467702000	-1.256790000
H	0.814729000	4.368406000	0.547875000
C	2.616546000	3.672292000	-0.444048000
C	3.243613000	2.735208000	0.405314000
H	2.630683000	2.158112000	1.110120000
C	4.629237000	2.528633000	0.340479000
H	5.098984000	1.789507000	1.008213000
C	5.415481000	3.255439000	-0.571825000
H	6.503033000	3.089876000	-0.625870000
C	4.800615000	4.194333000	-1.418857000
H	5.404184000	4.766989000	-2.140762000
C	3.410740000	4.396610000	-1.355780000
H	2.930895000	5.122211000	-2.032148000
C	-3.860013000	1.124867000	0.384534000
H	-4.362390000	0.847466000	-0.563102000
H	-4.469409000	0.779486000	1.240904000
C	-3.656073000	2.626457000	0.460714000
C	-4.350302000	3.409576000	1.404342000
H	-5.065055000	2.924966000	2.088217000
C	-4.129557000	4.795017000	1.490661000
H	-4.678290000	5.390765000	2.236381000
C	-3.202759000	5.416588000	0.635867000
H	-3.023923000	6.500742000	0.709482000
C	-2.505482000	4.641650000	-0.309187000
H	-1.776799000	5.117034000	-0.985089000
C	-2.730836000	3.259984000	-0.397576000
H	-2.176654000	2.652703000	-1.126087000

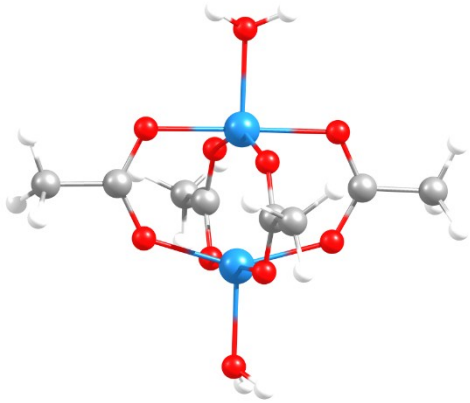
0:	0.00 cm**-1
1:	0.00 cm**-1
2:	0.00 cm**-1
3:	0.00 cm**-1
4:	0.00 cm**-1
5:	0.00 cm**-1

```
   6:        13.71 cm**-1
   7:        15.56 cm**-1
   8:        17.10 cm**-1
   9:        18.66 cm**-1
  10:        25.27 cm**-1
  11:        25.41 cm**-1
  12:        27.46 cm**-1
```

$[Zn_2(acetate)_4(OH_2)_2]$: There is a passing reference in the manuscript to the possibility of local TBP geometry for zinc paddlewheels with axial oxygen donors. Below is the optimised structure (usual ORCA protocol).

-4625.12659433 Eh

```
   0:         0.00 cm**-1
   1:         0.00 cm**-1
   2:         0.00 cm**-1
   3:         0.00 cm**-1
   4:         0.00 cm**-1
   5:         0.00 cm**-1
   6:        21.60 cm**-1
   7:        41.71 cm**-1
   8:        44.64 cm**-1
   9:        47.79 cm**-1
  10:        50.30 cm**-1
  11:        52.40 cm**-1
  12:        59.05 cm**-1
```



CuPCH3.2NHC: Symmetric TBP BS: ORCA (-4803.962857050633 Eh)

```
Cu      -0.000053000     -0.000236000     -1.489618000
Cu      -0.000041000     -0.000772000      1.486881000
O       -2.026397000     -0.056217000     -0.790021000
O        2.026286000      0.055745000     -0.789913000
O       -0.071567000      1.998499000     -1.479584000
O        0.071436000     -1.998947000     -1.479827000
C       -2.586337000     -0.099763000      0.339699000
C       -0.099627000      2.585526000     -0.342608000
O        1.998548000      0.074585000      1.476602000
O       -1.998613000     -0.076251000      1.476480000
O        0.060840000     -2.025830000      0.786678000
O       -0.060516000      2.024710000      0.786904000
C        2.586247000      0.098699000      0.339819000
C        4.105182000      0.224059000      0.373873000
H        4.556236000     -0.414832000     -0.409618000
H        4.377550000      1.275424000      0.144421000
H        4.512971000     -0.038909000      1.367054000
C        0.099796000     -2.586286000     -0.343021000
C       -0.576745000     -0.373112000     -5.684691000
H       -1.178079000     -0.765092000     -6.511331000
N       -0.908170000     -0.585104000     -4.349109000
C       -0.000086000      0.000039000     -3.517696000
N        0.907872000      0.585687000     -4.348893000
C        0.576245000      0.374506000     -5.684551000
H        1.177457000      0.766983000     -6.511044000
C        0.376936000     -0.573384000      5.682453000
H        0.772203000     -1.172325000      6.509264000
N        0.589469000     -0.904862000      4.346983000
C       -0.000072000      0.000103000      3.515239000
N       -0.589259000      0.906009000      4.346195000
```

C	-1.374225000	2.045278000	3.876868000
H	-1.144750000	2.932951000	4.496200000
H	-2.457312000	1.823277000	3.944246000
H	-1.105288000	2.239623000	2.822224000
C	-0.376118000	0.576054000	5.681949000
H	-0.771054000	1.175884000	6.508285000
C	2.051049000	1.365117000	-3.879804000
H	1.834132000	2.449272000	-3.946728000
H	2.244812000	1.094894000	-2.825345000
H	2.937360000	1.131745000	-4.499662000
C	-2.051310000	-1.364775000	-3.880331000
H	-2.244637000	-1.095500000	-2.825551000
H	-2.937811000	-1.130663000	-4.499640000
H	-1.834605000	-2.448903000	-3.948385000
C	1.373868000	-2.044903000	3.878632000
H	1.142356000	-2.932609000	4.497201000
H	2.457114000	-1.824270000	3.947896000
H	1.106388000	-2.238634000	2.823510000
C	0.225687000	-4.105164000	-0.377105000
H	1.278580000	-4.376845000	-0.154325000
H	-0.043160000	-4.513406000	-1.368449000
H	-0.408002000	-4.556296000	0.410458000
C	-0.225163000	4.104448000	-0.376171000
H	0.410852000	4.555208000	0.409745000
H	-1.277313000	4.376467000	-0.150348000
H	0.041173000	4.512807000	-1.368134000
C	-4.105278000	-0.225086000	0.373690000
H	-4.513029000	0.036717000	1.367189000
H	-4.556301000	0.414807000	-0.409009000
H	-4.377726000	-1.276146000	0.142952000

[Cu(acetate)$_2$(Me$_2$NHC)]: ORCA BP/SVP/D3/COSMO optimimised

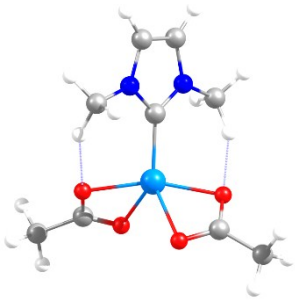
E(BP/SVP/D3/COSMO): -2401.958860580890 Eh

Gibbs correction: 0.17567433 Eh

G -2401.78318625

E(B3LYP/TZVP/D3/COSMO@BP/SVP/D3/COSMO geom): -2402.288238835526 Eh

C	-2.417553869	-4.119414482	4.567654140
H	-2.672623591	-4.947167996	5.236212400
C	-2.187009855	-1.955050198	3.928895937
C	-0.543089170	1.187242674	5.296194465
C	0.460683059	1.779139624	6.259469284
H	0.005096302	1.947115166	7.253877068
H	0.873026318	2.723228910	5.857859372
H	1.297149044	1.060210276	6.388958387
O	-1.427316362	0.365742431	5.761422147
O	-0.514074858	1.450139490	4.060415613
N	-2.552934846	-2.788969785	4.944709556
Cu	-2.235672089	0.003914734	3.922839485
C	-1.941479285	-4.114370970	3.279033574
H	-1.683122937	-4.936709510	2.605092011
C	-3.854737462	1.215607562	2.521687848
C	-4.864332034	1.828985947	1.583333892
H	-4.417408810	1.995345441	0.584240577
H	-5.257475315	2.776586705	1.994343404
H	-5.708126680	1.118586395	1.456093134
O	-3.066378102	0.298580585	2.071137235
O	-3.784757886	1.549371437	3.742984850
N	-1.814094330	-2.781106577	2.909141670
C	-3.090395453	-2.335027507	6.226487421



H	-4.186400058	-2.188599647	6.154897392
H	-2.876842985	-3.095237247	6.999528936
H	-2.602943531	-1.381746891	6.497074365
C	-1.285871444	-2.318773527	1.626497590
H	-0.189478719	-2.172703025	1.690237578
H	-1.505929027	-3.073896110	0.850220434
H	-1.775939290	-1.364772297	1.364520590

CuPCH3.2Me_2NHC:

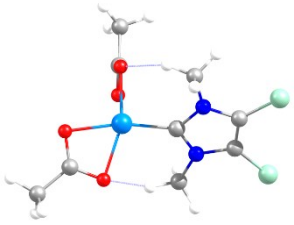
E(BP/SVP/D3/COSMO): -4803.96162140 Eh

Gibbs correction: 0.37932803 Eh

G -4803.58229337

E(B3LYP/TZVP/D3/COSMO@BP/SVP/D3/COSMO geom): -4804.60134186 Eh

[Cu(acetate)$_2$(Me_2NHCCl_2)]: ORCA BP/SVP/D3/COSMO optimimised

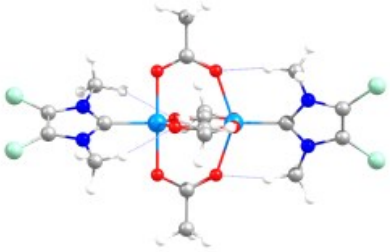


C	-1.875048112	-3.999883605	4.766817379
C	-2.297605654	-1.912581779	4.003152683
C	-0.691170304	0.814128516	5.175309794
C	0.358275842	1.212864200	6.198858007
H	-0.084891755	1.830332209	7.003364175
H	1.190323541	1.753264188	5.711219909
H	0.763430649	0.292435457	6.669413491
O	-1.872355830	0.536011669	5.638440949
O	-0.420228355	0.729583663	3.952611910
N	-2.372402645	-2.739391030	5.085304281
Cu	-2.715543148	-0.003195401	3.874101720
C	-1.466779407	-3.943161313	3.448295192
C	-4.014155022	1.344223200	2.330928068
C	-4.776998697	2.201897383	1.359792780
H	-4.226830507	2.246166446	0.398003935
H	-4.917466164	3.223115296	1.757631068
H	-5.762916333	1.739464699	1.151781118
O	-3.760583371	0.116556764	2.053091217
O	-3.597659849	1.808577638	3.447528399
N	-1.739959901	-2.654086662	3.002770739
C	-2.931944760	-2.357784044	6.381005846
H	-4.008125962	-2.613849562	6.427366354
H	-2.392385925	-2.895543120	7.181187817
H	-2.782739952	-1.269823322	6.499376622
C	-1.404840360	-2.131963784	1.679712922
H	-0.339072608	-1.834417946	1.645429792
H	-1.597031481	-2.908802417	0.917706588
H	-2.048505299	-1.255343917	1.489069672
Cl	-1.826804737	-5.311146467	5.859630276
Cl	-0.759148483	-5.156853124	2.477633999

0:	0.00 cm**-1
1:	0.00 cm**-1
2:	0.00 cm**-1
3:	0.00 cm**-1
4:	0.00 cm**-1
5:	0.00 cm**-1
6:	17.25 cm**-1
7:	22.16 cm**-1
8:	29.31 cm**-1
9:	37.04 cm**-1
10:	48.51 cm**-1
11:	57.96 cm**-1
12:	64.30 cm**-1

Electronic energy ... -3320.95749392 Eh
Final Gibbs free enthalpy ... -3320.80227212 Eh

CuPCH3.2Me$_2$NHCCl$_2$: ORCA BP/SVP/D3/COSMO optimimised



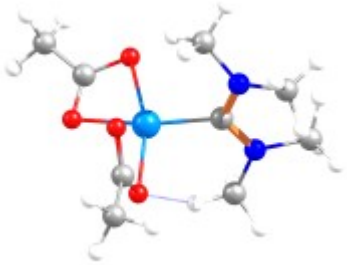
Cu	1.070148000	0.365584000	-0.440675000
O	-0.287938000	0.276618000	-2.074434000
O	1.225597000	-0.038565000	1.641283000
O	0.446884000	2.228275000	-0.039598000
O	1.690546000	-1.499733000	-0.838120000
C	-1.480071000	-0.107427000	-2.245173000
C	-0.732387000	2.358174000	0.438984000
Cu	-1.510945000	-0.704875000	0.519215000
O	-0.756388000	-0.854873000	2.370672000
O	-2.260622000	-0.552958000	-1.334855000
O	-0.292172000	-2.323354000	-0.119285000
O	-1.528281000	1.414439000	0.710261000
C	0.451478000	-0.470195000	2.542554000
C	0.977990000	-0.512082000	3.969752000
H	2.031742000	-0.851122000	3.976626000
H	0.954999000	0.517112000	4.385056000
H	0.358821000	-1.166249000	4.610592000
C	0.880002000	-2.453497000	-0.574337000
C	4.627886000	1.585566000	-2.422471000
N	3.397057000	0.940382000	-2.343301000
C	2.849554000	1.100149000	-1.103872000
N	3.743941000	1.853591000	-0.401075000
C	4.846156000	2.169219000	-1.190365000
C	-4.865121000	-2.780804000	2.103713000
N	-3.517451000	-2.634952000	1.787571000
C	-3.292951000	-1.432358000	1.183423000
N	-4.510657000	-0.820503000	1.118428000
C	-4.735929000	0.496144000	0.526996000
H	-5.379839000	1.097157000	1.196116000
H	-5.225937000	0.395789000	-0.460658000
H	-3.750170000	0.982143000	0.411383000
C	-5.496614000	-1.630302000	1.674857000
C	3.549365000	2.277768000	0.983217000
H	3.283987000	3.351828000	1.023085000
H	2.727976000	1.670680000	1.405138000
H	4.480179000	2.108740000	1.556437000
C	2.773479000	0.179092000	-3.422918000
H	1.717064000	0.011618000	-3.145087000
H	2.831945000	0.756417000	-4.364643000
H	3.287512000	-0.792372000	-3.555763000
C	-2.474207000	-3.617232000	2.071525000
H	-2.819589000	-4.622828000	1.766414000
H	-2.235463000	-3.623882000	3.152538000
H	-1.579512000	-3.330327000	1.489777000
C	1.399168000	-3.865393000	-0.804065000
H	1.690040000	-4.298453000	0.175790000
H	2.282590000	-3.868656000	-1.468542000
H	0.597338000	-4.501782000	-1.225317000
C	-1.216894000	3.782786000	0.666141000
H	-1.798824000	3.841056000	1.606015000
H	-1.896571000	4.061835000	-0.165972000
H	-0.374362000	4.498010000	0.689934000
C	-2.040934000	-0.072598000	-3.659463000
H	-3.144645000	-0.134198000	-3.658900000
H	-1.706278000	0.846051000	-4.178600000
H	-1.636829000	-0.940422000	-4.221437000

Cl	-5.523157000	-4.160261000	2.873841000
Cl	-7.149790000	-1.197696000	1.768781000
Cl	5.611479000	1.601412000	-3.822941000
Cl	6.173339000	3.105037000	-0.650145000

0:	0.00 cm**-1
1:	0.00 cm**-1
2:	0.00 cm**-1
3:	0.00 cm**-1
4:	0.00 cm**-1
5:	0.00 cm**-1
6:	10.91 cm**-1
7:	12.16 cm**-1
8:	19.29 cm**-1
9:	21.04 cm**-1
10:	23.38 cm**-1
11:	26.47 cm**-1
12:	35.43 cm**-1

Electronic energy ... -6641.95961441 Eh
Final Gibbs free enthalpy ... -6641.62129803 Eh

[Cu(acetate)$_2$(Me$_2$NCNMe$_2$)]: ORCA BP/SVP/D3/COSMO optimimised



C	-2.380271000	-1.983198000	3.964052000
C	-0.744381000	0.953796000	4.692893000
C	0.441220000	1.474243000	5.492880000
H	0.102648000	2.054025000	6.373141000
H	1.100712000	2.092220000	4.855997000
H	1.025724000	0.609076000	5.870743000
O	-1.762389000	0.539296000	5.378963000
O	-0.714559000	0.908317000	3.438661000
N	-2.815320000	-2.733438000	4.992862000
Cu	-2.919637000	-0.093176000	3.825615000
C	-4.598952000	1.095156000	2.517969000
C	-5.571412000	1.856078000	1.652439000
H	-5.027529000	2.248364000	0.767463000
H	-6.001596000	2.712838000	2.203355000
H	-6.373301000	1.188209000	1.284862000
O	-4.323490000	-0.129512000	2.249605000
O	-4.014665000	1.661189000	3.501979000
N	-1.531144000	-2.478917000	3.046572000
C	-3.514229000	-2.086517000	6.105549000
H	-4.613467000	-2.222889000	6.015095000
H	-3.182757000	-2.540339000	7.061231000
H	-3.260817000	-1.012368000	6.128131000
C	-1.334675000	-1.749599000	1.790286000
H	-0.409942000	-1.138324000	1.832594000
H	-1.260898000	-2.476639000	0.956701000
H	-2.200221000	-1.087809000	1.608063000
C	-0.559808000	-3.555048000	3.282711000
H	-0.835383000	-4.496905000	2.765172000
H	0.422195000	-3.220953000	2.891503000
H	-0.449393000	-3.745623000	4.363758000
C	-2.891146000	-4.200290000	4.997885000
H	-2.117719000	-4.661958000	5.645512000
H	-3.886854000	-4.491267000	5.388089000
H	-2.797650000	-4.593645000	3.971271000

0:	0.00 cm**-1
1:	0.00 cm**-1
2:	0.00 cm**-1

```
   3:         0.00 cm**-1
   4:         0.00 cm**-1
   5:         0.00 cm**-1
   6:        14.42 cm**-1
   7:        29.66 cm**-1
   8:        34.68 cm**-1
   9:        35.34 cm**-1
  10:        43.18 cm**-1
  11:        56.19 cm**-1

Electronic energy                ...  -2404.34561909 Eh
Final Gibbs free enthalpy        ...   -2404.12934639 Eh
```

CuPCH3.2Me$_2$NCNMe$_2$: ORCA BP/SVP/D3/COSMO optimimised

Cu	1.074386000	0.575893000	-0.562988000
O	-0.507920000	0.411698000	-2.056347000
O	1.140861000	-0.005998000	1.536210000
O	0.377423000	2.422275000	-0.168534000
O	1.757215000	-1.270880000	-0.983068000
C	-1.656280000	-0.082612000	-2.226610000
C	-0.790680000	2.487812000	0.358032000
Cu	-1.617875000	-0.676561000	0.529574000
O	-0.827659000	-0.758180000	2.368859000
O	-2.397150000	-0.595710000	-1.318785000
O	-0.203196000	-2.148490000	-0.262632000
O	-1.508874000	1.506455000	0.686732000
C	0.402370000	-0.412801000	2.470629000
C	1.011580000	-0.502234000	3.868343000
H	1.933508000	-1.116888000	3.831128000
H	1.310397000	0.513494000	4.199600000
H	0.304079000	-0.934945000	4.599518000
C	0.971674000	-2.244189000	-0.710505000
N	3.285546000	1.178425000	-2.449566000
C	2.904859000	1.262665000	-1.160832000
N	3.801189000	1.614090000	-0.212935000
N	-3.317167000	-2.608226000	1.976035000
C	-3.346849000	-1.484026000	1.231906000
N	-4.530102000	-0.898334000	0.958373000
C	-4.577733000	0.484846000	0.485307000
H	-5.297779000	1.058968000	1.106593000
H	-4.915416000	0.521464000	-0.571389000
H	-3.578029000	0.948460000	0.564155000
C	3.320909000	2.097238000	1.083332000
H	3.938240000	2.965126000	1.395936000
H	2.265973000	2.405833000	0.990365000
H	3.390387000	1.302014000	1.854206000
C	2.426297000	0.509350000	-3.426752000
H	1.423732000	0.334361000	-2.996019000
H	2.336929000	1.143013000	-4.333283000
H	2.864069000	-0.466717000	-3.724824000
C	-2.126793000	-3.458126000	1.982601000
H	-2.427827000	-4.509217000	1.786045000
H	-1.623361000	-3.412626000	2.970728000
H	-1.419859000	-3.128579000	1.200040000
C	1.537654000	-3.644898000	-0.927939000
H	1.785384000	-4.084617000	0.060892000
H	2.453200000	-3.624786000	-1.547654000
H	0.773522000	-4.295880000	-1.395942000
C	-1.353647000	3.888413000	0.579302000
H	-1.793018000	3.962666000	1.593632000
H	-2.174855000	4.060909000	-0.147306000

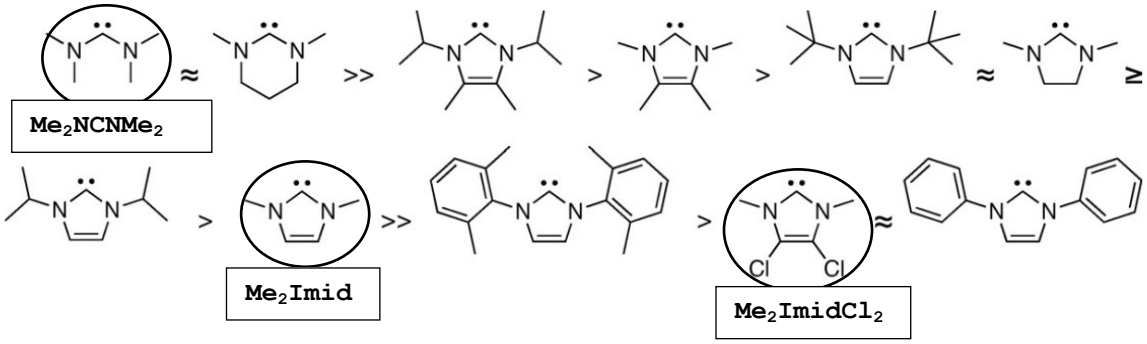
H	-0.582529000	4.668608000	0.441385000
C	-2.216904000	-0.105071000	-3.645871000
H	-3.306539000	-0.293477000	-3.651833000
H	-1.989903000	0.848949000	-4.160480000
H	-1.712528000	-0.914956000	-4.213719000
C	-4.314989000	-2.966817000	2.991721000
H	-4.966414000	-3.809589000	2.679348000
H	-3.774082000	-3.275775000	3.909302000
H	-4.941487000	-2.092814000	3.240395000
C	-5.816506000	-1.601964000	0.879809000
H	-5.655754000	-2.692474000	0.825351000
H	-6.487640000	-1.370612000	1.733191000
H	-6.325986000	-1.281080000	-0.051563000
C	5.234754000	1.293630000	-0.236137000
H	5.875253000	2.190047000	-0.373010000
H	5.496838000	0.831917000	0.738072000
H	5.457183000	0.558721000	-1.028111000
C	4.484232000	1.807917000	-3.020075000
H	5.309552000	1.086296000	-3.193749000
H	4.207447000	2.250491000	-3.997410000
H	4.838694000	2.618798000	-2.360653000

0:	0.00 cm**-1
1:	0.00 cm**-1
2:	0.00 cm**-1
3:	0.00 cm**-1
4:	0.00 cm**-1
5:	0.00 cm**-1
6:	22.39 cm**-1
7:	25.85 cm**-1
8:	27.41 cm**-1
9:	31.82 cm**-1
10:	33.16 cm**-1
11:	37.08 cm**-1
12:	37.43 cm**-1

Electronic energy ... -4808.72368940 Eh
Final Gibbs free enthalpy ... -4808.26396323 Eh

Reaction energy CuPCH3.2L → 2[Cu(acetate)$_2$(L)]

The three carbenes (circled) were chosen based on the computational study of Magill et al.[5] wich ranked a series of carbenes from most basic (Me_2NCNMe_2) to least basic ($Me_2ImidCl_2$ is equal least basic).



In the table below, a positive value indicates the paddlewheel structure is computed to have a lower energy than two monomers. The $Me_2ImidCl_2$ ligand gave the largest CPW electronic stabilisation which is why some of the entries in

the table are labelled NC (not calculated). The estimation of the Gibbs free energy contributions is based on the relevant BP/SVP/D3/COSMO results. According to the computational study of Vogiatzis et al.[6], post-Hartree-Fock methods like CASSCF and CASPT2 which would be expected to be quite accurate actually perform worse for the calculation of the exchange coupling parameters for copper acetate than hybrid or double-hypbrid DFT-based methods. In fact, the double hybrid B2PLYP gives the best agreement and we have included this method in the results below with a larger double-polarisation def2-TZVPP basis.

Carbene	**Me_2Imid**	**Me_2NCNMe_2**	**Me_2ImidCl_2**
DelE: BP/SVP (kcal)	25.0	20.4	28.0
DelG: BP/SVP (kcal)	8.4	3.3	10.5
DelE: B3LYP/TZVP (kcal)	15.6	NC	15.7
DelG: B3LYP/TZVP (kcal)	-1.0	NC	-1.8*
DelE: B2PLYP/TZVPP (kcal)	NC	NC	15.8

* Broken symmetry energy (BP/SVP/D3/COSMO structure)
E(High-Spin)-E(BrokenSym)= 0.0206 eV 165.890 cm**-1 (ANTIFERROMAGNETIC coupling)

The calculations above suggest that the CPW systems may be slightly thermodynamically unstable. This does not preclude their preparation since metastablity is fundamental in chemistry. The question is whether there is a significant barrier to the dissociation of the CPW and this, in turn, depends on the pathway. One way to generate two monomers from the CPW dimer would be to increase the Cu-Cu separation. BP/SVP/D3/COSMO constrained optimisations show that lengthening the Cu-Cu distance – all other degrees of freedom are allowed to relax - from its equilibrium value of 3.015 Å in 0.1 Å steps increases the electronic energy. By 3.31 Å, the increase is 3.0 kcal mol^{-1} and by 3.51 Å the increase is 6.8 kcal mol^{-1} relative to the lowest energy value. This dissociation pathway is therefore not viable.