

Supporting information

N-acetylserotonin and 6-hydroxymelatonin against Oxidative Stress: Implications for the Overall Protection Exerted by Melatonin

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Table 1S. Imaginary frequencies (cm⁻¹).

	6OHM		NAS	
	PE	W	PE	W
RAF-C6		332.5		
HT-C4		1469.8		
HT-O2	1719.5	2948.2	1699.9	2421.5

*W=aqueous solution, PE= pentyl ethanoate (lipid) solutions

Table 2S. Gibbs energies of activation, at 298.15 K (kcal/mol).

	6OHM		NAS	
	PE	W	PE	W
RAF-C6	20.10	9.87	19.10	20.04
HT-C4	16.73	13.81	16.91	16.52
HT-O2	21.13	11.21	22.00	20.56

*W=aqueous solution, PE= pentyl ethanoate (lipid) solutions

Table 3S. Tunneling corrections, at 298.15 K.

	6OHM		NAS	
	PE	W	PE	W
RAF-C6		1.00		
HT-C4		10.83		
HT-O2	22.59	86.54	18.30	74.31

*W=aqueous solution, PE= pentyl ethanoate (lipid) solutions

Details on the calculations of each individual rate constant

The rate constants (k) were calculated using conventional transition state theory as:

$$k = \frac{k_B T}{h} e^{-(\Delta G^\ddagger)/RT} \quad (1)$$

where k_B and h are the Boltzmann and Planck constants, T is the temperature (K), and $\Delta G^\ddagger$ is the Gibbs free energy of activation, which is calculated as the G difference between transition states and reactants for RAF and HAT reaction paths.

For the electron transfer reactions the barriers were obtained using the Marcus theory as:

$$\Delta G_{ET}^\ddagger = \frac{\lambda}{4} \left(1 + \frac{\Delta G_{ET}^0}{\lambda} \right)^2 \quad (2)$$

In this equation λ is calculated as:

$$\lambda \approx \Delta E_{ET} - \Delta G_{ET}^0 \quad (3)$$

where ΔE_{ET} is the non-adiabatic energy difference between reactants and vertical products. This approach is similar to that previously used by Nelsen and co-workers^{1,2} for a large set of reactions.

The standard state was changed to 1M according to:

$$\Delta G^{1M} = \Delta G^{1atm} - RT \ln(V_M) \quad (4)$$

where V_M represents the molar volume, R is the gas constant and T the temperature in K.

In addition, the free volume correction to liquid phase proposed by Benson³ has also been included:

$$\Delta G^{sol} \cong \Delta G^{gas} - RT \left\{ \ln \left[n 10^{(2n-2)} \right] - (n-1) \right\} \quad (5)$$

The limit imposed by diffusion has also been taken into account. To that purpose we used the Collins-Kimball theory:⁴

¹ S. F. Nelsen, S. C. Blackstock, Y. Kim, *J. Am. Chem. Soc.* **1987**, *109*, 677–682.

² S. F. Nelsen, M. N. Weaver, Y. Luo, J. R. Pladziewicz, L. K. Ausman, T. L. Jentzsch, J. J. O'Konek, *J. Phys. Chem. A* **2006**, *110*, 11665–11676.

³ S. W. Benson, *The Foundations of Chemical Kinetics*; Krieger: Florida, 1982.

⁴ F. C. Collins, G. E. Kimball, *J. Colloid Sci.* **1949**, *4*, 425–437.

$$k_{app} = \frac{k_D k}{k_D + k} \quad (6)$$

where k is the thermal rate constant, obtained from TST calculations, and k_D is the steady-state Smoluchowski⁵ rate constant for an irreversible bimolecular diffusion-controlled reaction:

$$k_D = 4\pi R_{AB} D_{AB} N_A \quad (7)$$

where R_{AB} denotes the reaction distance, N_A is the Avogadro number, and D_{AB} is the mutual diffusion coefficient of the reactants A (free radical) and B (scavenger). D_{AB} is calculated from D_A and D_B according to reference,⁶ D_A and D_B are estimated from the Stokes–Einstein approach:^{7,8}

$$D_{A \text{ or } B} = \frac{k_B T}{6\pi\eta a_{A \text{ or } B}} \quad (8)$$

where k_B is the Boltzmann constant, T is the temperature, η denotes the viscosity of the solvent, and a is the radius of the solute.

More details on the used methodology, and on how these equations are obtained can be found elsewhere.⁹

⁵ M. Smoluchowski, *Z. Phys. Chem.* **1917**, 92, 129–168.

⁶ D. G. Truhlar, *J. Chem. Ed.*, 1985, **62**, 104–106.

⁷ A. Einstein, *Ann. Phys.* **1905**, 17, 549–560.

⁸ G. G. Stokes, *Mathematical and Physical Papers* Cambridge University Press: Cambridge, 1903, Vol. 3, pp. 55.

⁹ A. Galano, J. R. Alvarez-Idaboy, *J. Comput. Chem.* **2013**, 34, 2430–2445.

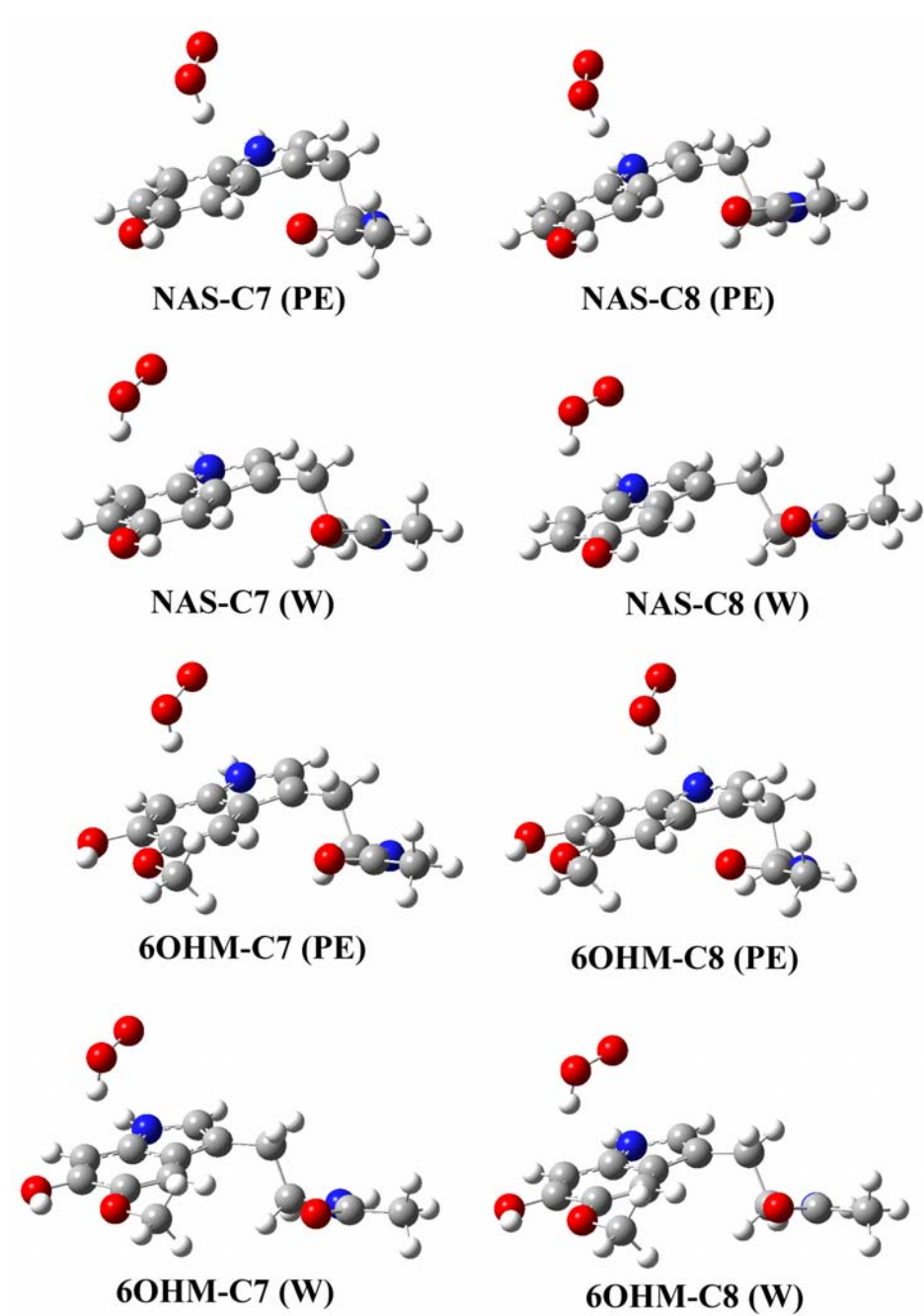


Figure 1S. Non-bonded complexes obtained when searching for adducts at sites C7 and C8.

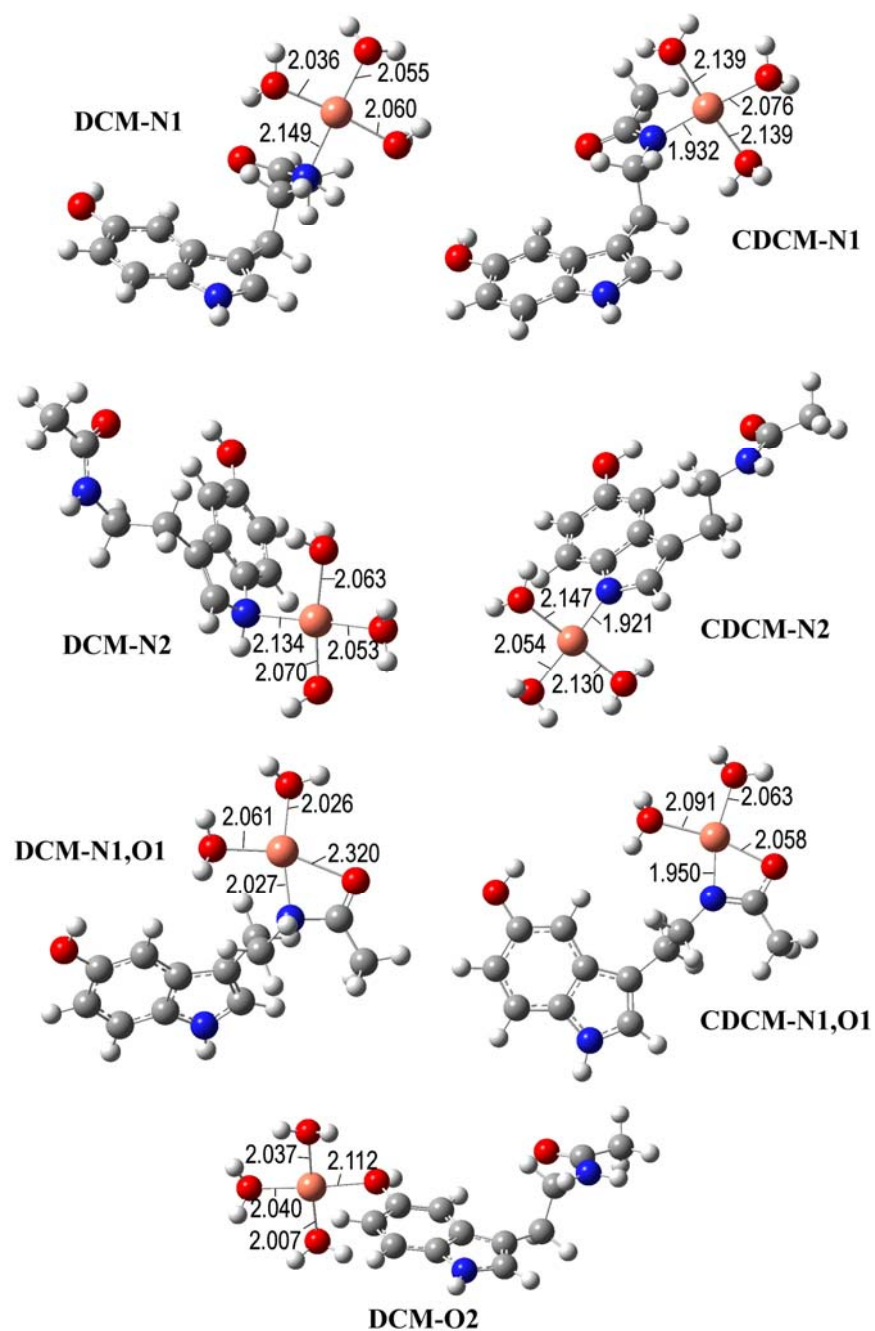


Figure 2S. Optimized geometries of the stable Cu^{2+} complexes with NAS yielded by endergonic reactions. Distances are reported in Å.

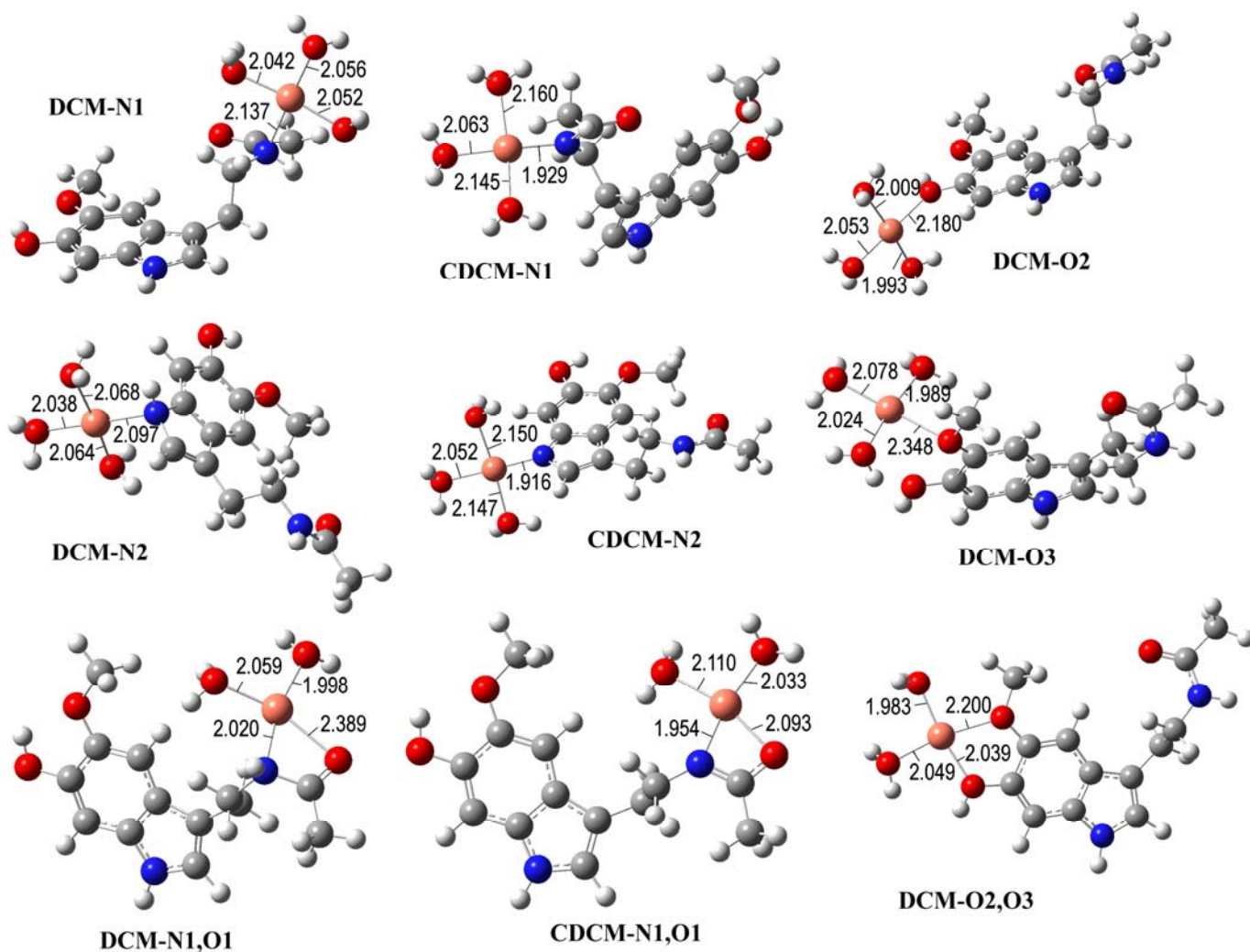


Figure 3S. Optimized geometries of the stable Cu^{2+} complexes with 6OHM yielded by endergonic reactions. Distances are reported in Å.

Cartesian coordinates of the transition states

NAS, TS-HAT-O2 (W)

\\0,2\C,2.2304303821,-1.0250305328,-0.7939252028\C,3.4420
187078,-0.3536430927,-0.4702486563\C,3.4367261891,0.9667644511,-0.0801
596238\C,2.191053224,1.6185632693,0.0001452219\C,0.9689171133,0.964647
0767,-0.307984024\C,0.9898769021,-0.3697919111,-0.7122453687\H,4.35484
48572,1.4876802243,0.1611529292\H,0.0849263872,-0.9111492015,-0.962763
2067\N,1.8874912872,2.8970722848,0.3568130529\H,2.5557421539,3.6038432
084,0.6286278405\O,2.2822330402,-2.3112529242,-1.204919245\C,-0.090915
7824,1.9247477525,-0.112824407\C,0.5203414737,3.0810631812,0.291505625
2\H,0.0892357157,4.0385053203,0.5393261648\C,-1.5556887102,1.665946021
8,-0.2796601623\H,-2.1035099673,2.6103329688,-0.2848810079\H,-1.740742
2579,1.1663889066,-1.2344533896\C,-2.0902526288,0.7776575541,0.8521492
227\H,-1.4887249547,-0.1272365517,0.9387052613\H,-2.0376647198,1.31155
28811,1.7994424322\N,-3.4759222641,0.3850559972,0.643017515\H,-4.20824
94768,0.9336991711,1.0690040897\C,-3.8230864905,-0.6166011363,-0.17526
77982\C,-5.2928412774,-0.8907224465,-0.3352422592\H,-5.9127174119,-0.1
937410222,0.2266593145\H,-5.5454995076,-0.8307033277,-1.3947264139\H,-
5.4936288136,-1.9087475984,0.0025018129\O,-2.9714793696,-1.3072554401,
-0.771314672\H,4.3684284392,-0.9087287323,-0.5460475552\H,2.0044831224
, -2.9428185547,-0.3897356556\O,1.677839806,-3.4166260493,0.8720905168\
O,1.2966598038,-2.2537671977,1.4612321229\H,2.1033863679,-1.9040858702
,1.8873388758\\

NAS, TS-HAT-O2 (PE)

\\0,2\C,0,-2.366178379,1.8575326728,-
0.0165291848\C,0,-3.6382992171,1.2389139783,0.168269862\C,0,-3.7711973
629,-0.1309110056,0.1793766333\C,0,-2.6041119897,-0.900126119,0.009243
5548\C,0,-1.3245186883,-0.3119073081,-0.1680251238\C,0,-1.2058388169,1
.0789437158,-0.1811567316\H,0,-4.7383339934,-0.601408935,0.3096840034\
H,0,-0.2517961812,1.5751649774,-0.3153759347\N,0,-2.4369373789,-2.2524
214767,-0.0263578019\H,0,-3.1734946534,-2.9353274764,0.0641784048\O,0,
-2.2914874721,3.1886135838,-0.0514627569\C,0,-0.3748695493,-1.39032973
97,-0.3113497225\C,0,-1.1019845502,-2.5467999132,-0.2181472537\H,0,-0.
7729278289,-3.5727530383,-0.2798811854\C,0,1.1052325816,-1.2500574633,
-0.492344602\H,0,1.536887521,-2.2121189326,-0.7798382617\H,0,1.3198033
7,-0.5369506197,-1.2924051946\C,0,1.790559342,-0.7514945022,0.78891745
7\H,0,1.3365634924,0.1844363622,1.1154010269\H,0,1.6737684898,-1.48525
15384,1.5869032488\N,0,3.2117896069,-0.5207271294,0.594955629\H,0,3.86
55808341,-1.2465441217,0.8426362187\C,0,3.6794786787,0.6107605144,0.02
07568754\C,0,5.1777942376,0.7049096867,-0.1441782558\H,0,5.4065329732,
0.8019850742,-1.2067763685\H,0,5.5268507671,1.6092427911,0.356205556\H
,0,5.7075262321,-0.1580879932,0.2598818507\O,0,2.9304705439,1.51726185
13,-0.3447296633\H,0,-4.4993391848,1.8846265509,0.2884721657\H,0,-1.96

8557632,3.5558516039,0.9218098868\O,0,-1.6704278314,3.6392947013,2.221
4928779\O,0,-1.286297463,2.356312304,2.4647221266\H,0,-2.0939332378,1.
9152970546,2.7899339434\\

6OHM, TS-RAF-C6 (W)

\\0,2\C,0,1.876186,1.685626,0.033844\C,0,3.102448,1.055338,-0.334315\C
,0,3.169323,-0.285247,-0.664586\C,0,1.974722,-1.003343,-0.618296\C,0,0
.74247,-0.400608,-0.256959\C,0,0.69934,0.975671,0.075399\H,0,4.114335,
-0.736349,-0.938344\H,0,-0.237272,1.440792,0.35299\N,0,1.727652,-2.328
887,-0.90564\H,0,2.438526,-3.023625,-1.081504\O,0,2.017381,3.017151,0.
32593\C,0,-0.250344,-1.40728,-0.300414\C,0,0.417628,-2.613104,-0.61507
8\C,0,-1.703761,-1.25726,0.000163\H,0,-2.161537,-2.240551,0.123851\H,0
, -1.833488,-0.704561,0.935496\C,0,-2.429201,-0.496271,-1.120389\H,0,-1
.926273,0.449072,-1.321826\H,0,-2.425818,-1.084397,-2.036319\N,0,-3.81
4826,-0.213682,-0.780003\H,0,-4.530966,-0.860861,-1.075597\C,0,-4.1664
13,0.805548,0.01501\C,0,-5.626894,0.941185,0.344678\H,0,-5.743823,0.87
376,1.42763\H,0,-5.966558,1.928965,0.029838\H,0,-6.236904,0.176402,-0.
133699\O,0,-3.327863,1.614508,0.461821\H,0,-0.028065,-3.536858,-0.9468
05\O,0,0.512215,-3.390105,1.278507\O,0,1.474632,-2.63993,1.948283\H,0,
2.320101,-2.978737,1.6083\C,0,0.827454,3.729133,0.677113\H,0,0.106382,
3.688464,-0.140983\H,0,0.389979,3.311444,1.585104\H,0,1.136363,4.75565
9,0.850986\O,0,4.245007,1.80412,-0.358563\H,0,4.026503,2.717075,-0.104
457\\

6OHM, TS-HAT-O2 (W)

\\0,2\C,0,-2.1162941409,1.1046475681,-0.0893727
96\C,0,-3.3192248978,0.3360146383,0.1042904347\C,0,-3.2836804249,-1.05
84920744,0.1653916191\C,0,-2.0489053045,-1.6718127969,0.0193907269\C,0
, -0.8520947588,-0.9253220168,-0.1691815706\C,0,-0.8916427475,0.4843851
097,-0.2190746237\H,0,-4.2032968069,-1.611589234,0.3090730537\H,0,0.02
12101816,1.0485156152,-0.3557054242\N,0,-1.7051668484,-3.0042258023,0.
0151401887\H,0,-2.3446566257,-3.7761047151,0.1273543997\O,0,-2.3170852
082,2.447347957,-0.1125293028\O,0,-4.5010330769,0.9810363377,0.1618597
505\H,0,-4.5281365927,1.5548849354,1.0353650949\C,0,0.2191538809,-1.86
29745807,-0.2864133716\C,0,-0.3526945649,-3.1123782533,-0.1662571702\H
,0,0.1164312297,-4.0836724446,-0.2030388048\C,0,1.6665243322,-1.524949
5589,-0.471357834\H,0,2.2203108097,-2.4055267424,-0.8028621257\H,0,1.7
700248876,-0.7568780803,-1.2432000043\C,0,2.2852508096,-0.9951867789,0
.8291974874\H,0,1.6587693253,-0.207967967,1.2491395662\H,0,2.360480710
8,-1.7961921188,1.5628121973\N,0,3.6214144948,-0.4530564939,0.62814759
33\H,0,4.4207940362,-1.043953015,0.8023862287\C,0,3.8302790803,0.78186
6043,0.1554786493\C,0,5.2588999977,1.2137760657,-0.0253290887\H,0,5.44
27011843,2.076761857,0.6169599152\H,0,5.9700180967,0.425460589,0.21714
53659\H,0,5.4003211944,1.5269241493,-1.0605600948\O,0,2.8868907965,1.5

54360938,-0.1130105679\C,0,-1.1555907525,3.2736960643,-0.2369666281\H,
0,-0.4784654373,3.1038560385,0.6018041163\H,0,-0.6449908312,3.07526780
77,-1.180281974\H,0,-1.5194971248,4.296839324,-0.2204144828\O,0,-4.274
0089153,1.9301078936,2.4189799345\O,0,-3.1354380247,1.2198903253,2.615
7730324\H,0,-3.4257791642,0.3650629067,2.9891732197\\

6OHM, TS-HAT-C4 (W)

\\0,2\C,0,-2.383550861,1.0229541186,-0.56696853
84\C,0,-3.4291956845,0.1037011716,-0.291347137\C,0,-3.1722250857,-1.17
21938924,0.166094201\C,0,-1.8293319122,-1.5169036526,0.3464862103\C,0,
-0.7772087656,-0.6215494725,0.088861344\C,0,-1.0585157316,0.6743273889
, -0.3814242173\H,0,-3.9843741955,-1.8593098891,0.3668958217\H,0,-0.257
6098537,1.3711117056,-0.5907004779\N,0,-1.2702265019,-2.7064723176,0.7
746429116\H,0,-1.7876533622,-3.5336334192,1.0339655661\O,0,-2.82916948
9,2.2401305052,-1.0171739044\O,0,-4.7315090191,0.4975056975,-0.4884193
375\H,0,-4.73013372,1.4119136211,-0.817519638\C,0,0.4577446772,-1.3165
776617,0.3829647956\C,0,0.0843856841,-2.5964279749,0.7873999647\H,0,0.
6958189004,-3.4318945631,1.0894449397\C,0,1.7982201434,-0.8055129159,0
.1769704619\H,0,1.9704573173,-0.9284782773,-1.0470129549\H,0,1.8805054
167,0.275715249,0.304034347\C,0,2.9363627209,-1.5748339526,0.824644634
6\H,0,2.8925315123,-1.4786857385,1.9107503325\H,0,2.8669884084,-2.6330
463142,0.5775889985\N,0,4.2394366104,-1.112274262,0.3720104509\H,0,4.6
668914512,-1.5793487991,-0.4141198283\C,0,4.8309382457,-0.0140399019,0
.8598937949\C,0,6.1555638315,0.3659399476,0.2589365778\H,0,6.086999567
7,1.3855965938,-0.1226147457\H,0,6.9095598191,0.3502070162,1.047832266
\H,0,6.4569595332,-0.3049247255,-0.5445347578\O,0,4.3236917162,0.65652
48134,1.7812111875\C,0,-1.8353370354,3.2150607492,-1.3422232034\H,0,-1
.2452521875,3.4641894568,-0.4589681567\H,0,-1.1862959962,2.8444298793,
-2.1372469193\H,0,-2.3796615828,4.0905081579,-1.6843911234\O,0,1.94706
02641,-1.2391663883,-2.3717543161\O,0,1.0156321187,-2.2660856618,-2.38
55070665\H,0,0.1550202754,-1.8108291513,-2.4034644437\\

6OHM, TS-HAT-O2 (PE)

\\0,2\C,0,1.61436,-0.724315,-0.664885\C,0,2.776189,0.121811,
-0.512631\C,0,2.636818,1.496533,-0.289345\C,0,1.350714,2.013188,-0.232
85\C,0,0.20199,1.185709,-0.365973\C,0,0.338685,-0.200613,-0.58229\H,0,
3.526563,2.104772,-0.183775\H,0,-0.543489,-0.821859,-0.676832\N,0,0.90
4612,3.302108,-0.044714\H,0,1.488928,4.114665,0.070946\O,0,1.90821,-2.
021933,-0.874399\O,0,3.98717,-0.410407,-0.631382\H,0,4.12233,-1.133936
,0.141434\C,0,-0.947531,2.031081,-0.248548\C,0,-0.466877,3.306341,-0.0
53739\H,0,-1.010913,4.229863,0.075074\C,0,-2.370239,1.566347,-0.304682
\H,0,-3.047738,2.416151,-0.417619\H,0,-2.508084,0.915166,-1.172565\C,0
, -2.748363,0.767562,0.952846\H,0,-1.965435,0.042874,1.17728\H,0,-2.850
899,1.43412,1.809233\N,0,-3.995316,0.039957,0.791005\H,0,-4.853966,0.4
44319,1.130065\C,0,-4.040736,-1.139098,0.133221\C,0,-5.399879,-1.78326

,0.005465\H,0,-5.340675,-2.802069,0.390366\H,0,-6.180795,-1.240335,0.5
38246\H,0,-5.660423,-1.840374,-1.052954\O,0,-3.028882,-1.663183,-0.338
361\C,0,0.817488,-2.938786,-0.887318\H,0,0.269671,-2.896116,0.056607\H
,0,0.143112,-2.728094,-1.720256\H,0,1.260186,-3.923134,-1.013891\O,0,4
.113805,-1.656551,1.433502\O,0,2.905929,-1.18941,1.854802\H,0,3.120979
,-0.393577,2.375688\\

Cartesian coordinates of relevant Cu complexes

Cu(II), 6OHM, DCM-O1

\\C,-1.7318982198,1.3868444751,-0.3503268767\C,-2.9734772787
,0.7992381356,0.0255651188\C,-3.0739300133,-0.5481599333,0.3196449968\
C,-1.9051928692,-1.316163999,0.2338304585\C,-0.6627090164,-0.758491333
4,-0.1414325861\C,-0.5826750743,0.6185331145,-0.4387173176\H,-4.031425
8948,-0.97717205,0.6008526903\H,0.3631450913,1.0618357722,-0.732588612
1\N,-1.7044856211,-2.655854652,0.4552279553\H,-2.4160500277,-3.3191435
131,0.7255340401\O,-1.8104875291,2.7329101368,-0.5967394196\O,-4.09874
06312,1.5826839631,0.0950701958\H,-3.8591129191,2.4877894383,-0.165613
6864\C,0.3042201974,-1.8244095492,-0.1410550328\C,-0.3808463298,-2.958
0513442,0.2275326497\H,-0.0264790016,-3.9740339517,0.3480600489\C,1.75
94861371,-1.6867205767,-0.4514276722\H,2.1806012497,-2.6516198015,-0.7
519516022\H,1.8849453813,-1.0061084382,-1.3013857728\C,2.5614267255,-1
.1339135127,0.7337957316\H,2.00925363,-0.3372904753,1.2340103666\H,2.7
509633428,-1.9166799292,1.4698359342\N,3.8529594292,-0.5901035436,0.33
45746356\H,4.6596953574,-1.1996652236,0.3327218386\C,4.00383283,0.6397
930389,-0.1509885723\C,5.3515718084,1.0720186017,-0.6193904896\H,5.279
1282976,1.3759992412,-1.6678502955\H,5.6696362521,1.9448895881,-0.0426
022625\H,6.1009056115,0.2856182433,-0.5237109664\O,3.0028253934,1.4089
136622,-0.1946268077\C,-0.6428518289,3.409813643,-1.0404901453\H,0.156
7757512,3.3394850063,-0.2950309799\H,-0.30229213,3.0024240617,-1.99816
98047\H,-0.9326622495,4.4528350656,-1.1687078332\Cu,2.9775990804,3.259
3410703,-0.853098877\O,3.6920438523,3.8582340463,0.9814727247\H,3.3676
100418,4.7469398801,1.2021318006\H,3.2863175177,3.2774304599,1.6467739
17\O,2.3594504423,2.6146809247,-2.7286980669\H,3.1170776522,2.13613923
22,-3.1056657246\H,1.7029160001,1.9169813758,-2.5593757992\O,2.6619960
195,5.1583053573,-1.5341699186\H,2.6536320001,5.7846432017,-0.79117903
76\H,1.7537675121,5.1816080308,-1.8821728839\\

Cu(II), 6OHM, CDCM-O2

\\C,0.2784964551,-0.7513109078,-0.8273924533\
C,1.4230503988,0.1338057323,-0.8718783233\C,1.2172610133,1.516642274,-
0.7291478581\C,-0.0823699485,1.9917663266,-0.5632967561\C,-1.204336328

3,1.1284210988,-0.5403056806\C,-1.0088038835,-0.2647549792,-0.67766746
94\H,2.0738080406,2.1851471498,-0.7594808397\H,-1.8632829273,-0.933641
7612,-0.6598904303\N,-0.5506760348,3.2764903951,-0.4135528458\H,0.0170
961332,4.1111447871,-0.4054784185\O,0.5897995593,-2.0752779953,-0.9595
944343\O,2.6275107931,-0.3684240134,-1.0655141224\C,-2.3723994482,1.94
49762318,-0.3780779811\C,-1.9189609594,3.2451984614,-0.3057652366\H,-2
.4784672637,4.165237837,-0.1911877208\C,-3.7907617978,1.4773795106,-0.
3073542626\H,-4.4679476208,2.3293217379,-0.4307084275\H,-3.9948841996,
0.7849358347,-1.1338523315\C,-4.1176791159,0.7682431554,1.0096081297\H
,-3.4002740008,-0.0318338326,1.2022832262\H,-4.054617058,1.4718490459,
1.8425326261\N,-5.4501031649,0.1890675398,1.0287657571\H,-6.2136940483
,0.7754787963,1.3346989945\C,-5.7479181061,-1.0276823588,0.5329942979\
C,-7.1928099689,-1.4354889674,0.5647150479\H,-7.545850416,-1.557174051
1,-0.4636854312\H,-7.2775791738,-2.4078604351,1.0569033442\H,-7.836604
5455,-0.7175599937,1.0763726396\O,-4.8758801603,-1.7904026233,0.074481
6196\C,-0.4708830749,-3.0168517596,-1.0030814631\H,-1.0503208024,-3.00
49463428,-0.0733925633\H,-1.1345340027,-2.823748128,-1.8527861836\H,0.
0000381729,-3.9927980326,-1.1235807274\Cu,3.9345452339,-0.3162851505,0
.3177689648\O,2.6815195467,-1.0235363149,1.956718775\H,1.7764836895,-0
.7217841201,1.7771273473\O,5.5058306294,-0.0617131505,1.6773343545\H,6
.3155808674,-0.3853259121,1.2515873619\O,5.4875693789,-0.0898757132,-1
.2959251534\H,6.0462210161,0.6714084674,-1.0754644892\H,2.9421239543,-
0.5392022401,2.75584608\H,4.9479325253,0.2203591246,-2.0397060244\H,5.
3700516426,-0.6666147226,2.4242960616\\

Cu(II), 6OHM, CDCM-O2,O3

\\C,0.925521,0.080541,-0.124399\C,1.73479,1.247801,0.044309\C,1.1157,2.
495734,0.091064\C,-0.279198,2.549332,-0.034187\C,-1.076791,1.394414,-0
.203911\C,-0.449555,0.129677,-0.247434\H,1.715611,3.393031,0.216909\H,
-1.03881,-0.773181,-0.375344\N,-1.122193,3.631928,-0.03324\H,-0.835714
,4.595286,0.055514\O,1.678234,-1.084321,-0.146908\O,3.058098,1.11931,0
.157143\C,-2.44593,1.828748,-0.312975\C,-2.41921,3.19858,-0.20292\H,-3
.232927,3.912025,-0.239502\C,-3.656165,0.970827,-0.495215\H,-4.503366,
1.593201,-0.803596\H,-3.488058,0.243568,-1.298848\C,-4.045396,0.212048
,0.774914\H,-3.227223,-0.42923,1.108817\H,-4.257461,0.919197,1.580316\
N,-5.22725,-0.615369,0.599989\H,-6.126661,-0.170998,0.719728\C,-5.2110
85,-1.86978,0.110094\C,-6.54485,-2.533024,-0.079433\H,-6.650569,-2.821
924,-1.128878\H,-6.572095,-3.450287,0.515869\H,-7.388766,-1.900325,0.2
02226\O,-4.151418,-2.469126,-0.156253\C,1.027492,-2.337675,-0.341264\H
,0.329134,-2.530981,0.477842\H,0.500306,-2.345873,-1.299287\H,1.813185
, -3.091054,-0.343133\Cu,3.739566,-0.640241,0.064793\O,5.674918,0.10147
8,0.295635\H,5.621567,1.059506,0.144542\H,6.22459,-0.228305,-0.433726\
O,4.382901,-2.583115,0.01917\H,4.82057,-2.731931,-0.835465\H,5.101574,
-2.667798,0.667626\\

Cu(II), NAS, DCM-O1

\\C,-2.111761 8359,1.2073183705,-0.2663506483\\C,-3.2998922358,0.4601109156,-0.117757
1559\\C,-3.2615142234,-0.926136967,-0.0602175716\\C,-2.0150884713,-1.553
1368956,-0.1513912725\\C,-0.8155542557,-0.8142037034,-0.2991704585\\C,-0
.8719949554,0.5921102303,-0.3594681899\\H,-4.1757267649,-1.5024383915,0
.0526230279\\H,0.0305127422,1.1903188027,-0.4727541004\\N,-1.6756141851,
-2.8860400494,-0.1274274361\\H,-2.3225530494,-3.6556659852,-0.035413134
8\\O,-2.2535656606,2.5799159582,-0.3094496475\\C,0.2641490488,-1.7599044
786,-0.3627830808\\C,-0.315263998,-3.0039114058,-0.2531741139\\H,0.14866
61245,-3.9825780628,-0.257202639\\C,1.7191936741,-1.4418545449,-0.48456
76481\\H,2.2756389456,-2.3374806297,-0.7795320415\\H,1.8750796945,-0.694
594502,-1.2733449483\\C,2.3023028311,-0.9021566094,0.8241101441\\H,1.697
9065247,-0.0782473434,1.2070959175\\H,2.3158393725,-1.6850659845,1.5843
548002\\N,3.6724977261,-0.4297536301,0.6739367977\\H,4.4239651649,-1.079
8529443,0.8607039368\\C,4.0014053322,0.7695262663,0.2028257059\\C,5.4480
419329,1.0984708346,0.042826407\\H,5.6067508921,1.5708419515,-0.9298638
569\\H,5.7315929398,1.8205568061,0.8138999893\\H,6.0877245608,0.21971750
77,0.1301812875\\O,3.0903289432,1.6028053062,-0.0703228904\\Cu,3.3517041
699,3.2588151849,-1.1029187999\\O,4.2953252792,4.1989806668,0.476061355
4\\H,4.8797400342,4.8931047395,0.1288864994\\H,3.6018937975,4.6907947735
,0.9469721213\\O,2.1031473598,2.4174878124,-2.5190319244\\H,2.5239163553
,2.4542372912,-3.3935555068\\H,2.0221196572,1.4684313484,-2.3226919251\\
O,3.504478161,4.8495735511,-2.3764673651\\H,4.1058615001,5.5161324693,-
2.0050153128\\H,2.6398338876,5.2936092362,-2.3989559446\\H,-4.2468725185
,0.9873579647,-0.0480521554\\H,-1.379505448,2.98895684,-0.4035929013\\

Cu(II), NAS, CDCM-O2

\\C,-2.7873605667,1.1954622353,1.0774763245\\C,-3.9008595644,
0.3215028277,1.2771646432\\C,-3.8616162605,-1.0109383899,0.9023879708\\C
, -2.6826498884,-1.4941136132,0.3181719596\\C,-1.5529754894,-0.662267437
1,0.1118432833\\C,-1.6164745144,0.6911108886,0.4847148272\\H,-4.71665990
4,-1.6636310948,1.0596514039\\H,-0.7668213915,1.3556950265,0.3398774282
\\N,-2.3593188304,-2.7463166127,-0.1408163951\\H,-2.9712397066,-3.549332
7488,-0.1342138001\\O,-2.8592211035,2.4695370874,1.4643970147\\C,-0.5293
138967,-1.4745346899,-0.4926077958\\C,-1.072298521,-2.7312840853,-0.623
9562578\\H,-0.6348079127,-3.632921226,-1.0342675255\\C,0.8526724495,-1.0
362787587,-0.8568185489\\H,1.3071789111,-1.7596147256,-1.5421907036\\H,0
.8130227272,-0.0757474205,-1.3847056072\\C,1.7505700467,-0.8781873256,0
.3739234934\\H,1.2694221068,-0.2359511745,1.1136037845\\H,1.9177319431,-
1.8505424951,0.8426033521\\N,3.0523375289,-0.3102202457,0.069782207\\H,3
.7921201063,-0.9416920355,-0.2035426687\\C,3.2998708519,1.0128208936,0
.0112746671\\C,4.6941453603,1.4220016735,-0.366928148\\H,4.6503241839,2.0
56330633,-1.2566861266\\H,5.1175490481,2.0224829471,0.4432606728\\H,5.35
46451265,0.575597638,-0.5639779258\\O,2.4277026334,1.8637855665,0.27048
00329\\Cu,-3.7602875224,3.7265369289,0.3712441486\\O,-2.7839549972,3.214
7065433,-1.5009568465\\H,-3.4658795996,3.1842104276,-2.1897799691\\O,-4.

4826999194,5.4732136118,-0.49268141\H,-5.4380487474,5.5331544033,-0.33
09805622\O,-5.4323981513,3.8643970699,1.8099033844\H,-5.479830729,2.97
3930407,2.1926415499\H,-2.4831579073,2.2948598324,-1.4175988931\H,-6.2
52090732,3.9472381311,1.2975689354\H,-4.4052964401,5.4091693193,-1.458
2261585\H,-4.7962424676,0.7305360372,1.7398442589\\

Cu(I), 6OHM, DCM-O1

\\C,2.0774343605,-1.8755607938,-0.1626033289\C,3.423
2401222,-2.3113083121,0.0022449572\C,4.4689067133,-1.4091002052,0.0745
985626\C,4.153091724,-0.0469762903,-0.0206688096\C,2.8268685572,0.4101
200987,-0.1864375532\C,1.7751203554,-0.5275135988,-0.2560263973\H,5.48
88442412,-1.761588325,0.1983254363\H,0.7502995416,-0.1952915746,-0.380
964728\N,4.9676180026,1.0574233168,0.0087865365\H,5.971779073,1.042782
7,0.1097656697\O,1.1656266751,-2.8974062716,-0.2171330469\O,3.69331406
18,-3.6545584595,0.0896801518\H,2.8545729651,-4.1409013999,0.025214034
7\C,2.8732132956,1.8466247107,-0.2655937819\C,4.1985988196,2.189836048
8,-0.1404776484\H,4.6660748876,3.1662492479,-0.1541152404\C,1.69994558
77,2.7546560372,-0.4485794243\H,2.0331490782,3.7392834611,-0.792567701
1\H,1.0473714841,2.3495529092,-1.2304146943\C,0.8737778143,2.919064231
4,0.8324291238\H,0.7426792622,1.9558151704,1.328244321\H,1.3832512575,
3.5830343004,1.533122596\N,-0.4512803412,3.4745735178,0.595078748\H,-0
.5750191185,4.4759121787,0.6493150502\C,-1.498600756,2.7330698698,0.21
86375935\C,-2.8037951476,3.4204693907,-0.0167520192\H,-3.1506727549,3.
1894285907,-1.0274715393\H,-3.5432176145,3.0228964605,0.6845415894\H,-
2.741087184,4.502765004,0.1050309485\O,-1.3734990064,1.4905313521,0.08
6770832\C,-0.2119501265,-2.5641283998,-0.3248139359\H,-0.5358670211,-1
.9742784062,0.5397186219\H,-0.4108832637,-2.0107872783,-1.2483460695\H
, -0.7468087001,-3.514282679,-0.3502398627\Cu,-2.6917605637,0.089458517
8,-0.2695979328\O,-6.4785493852,-0.7885444807,-0.3610158068\H,-6.46211
2638,0.1577517332,-0.153879555\H,-6.8803808204,-0.8253295818,-1.241749
4635\O,-3.2644293488,-3.4182045831,1.353804636\H,-2.3005707918,-3.4332
363156,1.4512800474\H,-3.5775471837,-3.0536993999,2.1948831445\O,-3.79
89422143,-1.5146757382,-0.6229851861\H,-4.7495371141,-1.2768570475,-0.
527889549\H,-3.6258857854,-2.1771237067,0.0847206731\\

Cu(I), 6OHM, CDCM-O2

\\C,0.1681454289,1.1690768512,-0.335189
5457\C,-1.0585507329,0.4077467833,-0.2261923842\C,-0.95683755,-0.98939
17667,-0.1797347428\C,0.3084589073,-1.59394611,-0.2356869049\C,1.49931
03409,-0.8463336356,-0.3344441308\C,1.4124242503,0.5639200939,-0.38519
77521\H,-1.8680435512,-1.579492168,-0.1021072806\H,2.3189260757,1.1563
727376,-0.4614699835\N,0.6602798038,-2.9228519962,-0.2123211965\H,0.01
56227712,-3.6979024561,-0.1688524428\O,-0.0185905556,2.5334256867,-0.3
793314336\O,-2.2082505649,1.058252783,-0.1775451709\C,2.5964327687,-1.
7793215114,-0.3744300975\C,2.0336138493,-3.032012194,-0.2988969429\H,2

.5041061984,-4.007300697,-0.3046551535\C,4.0518796391,-1.4462483044,-0.4582715411\H,4.626698385,-2.3463318754,-0.7036585403\H,4.2274408397,-0.7261872929,-1.267389476\C,4.5974858039,-0.849726507,0.8417197528\H,4.0165884229,0.026011988,1.136433631\H,4.5218197291,-1.580934387,1.6501008643\N,5.9904599621,-0.449831598,0.7410182938\H,6.692463217,-1.1590515539,0.8978292193\C,6.4044809997,0.7569824466,0.3100307321\C,7.8885514188,0.9565465187,0.1929832131\H,8.1291637837,1.2031057819,-0.8452965334\H,8.182644091,1.8111985249,0.8086719464\H,8.469641906,0.0825119984,0.4932714357\O,5.6090262784,1.6740167028,0.0287765122\C,1.128957092,3.3618483731,-0.4282836954\H,1.7662209043,3.2084162745,0.4498170658\H,1.7124366244,3.1816206122,-1.3381846339\H,0.7611187154,4.3886953769,-0.4338621034\Cu,-3.8998409561,0.1790672527,0.0210872039\O,-6.6868891837,0.2798346284,2.676361597\H,-6.0825465425,1.0005555505,2.9090386905\O,-5.6516302276,-0.6957396327,0.2706816774\H,-6.2663581405,-0.4210100119,-0.4472634806\O,-7.3564982454,0.0551482204,-1.8061766938\H,-7.8065448899,-0.7516642744,-2.0979854\H,-6.4780654331,-0.411841203,3.3215602377\H,-6.7683985676,0.2722327873,-2.5449191903\H,-6.0469130661,-0.3440037974,1.100725378\\

Cu(I), 6OHM, CDCM-O2,O3

\\C,0.6434125163,0.0086546101,-0.1435642727\C,1.4748237122,1.1773685422,0.0553374951\C,0.8374319328,2.4257879877,0.1206273129\C,-0.5564670733,2.5014995337,-0.0032769676\C,-1.3612842703,1.3582433672,-0.1913669452\C,-0.7347509878,0.0936468535,-0.2614657647\H,1.4413711308,3.3184304909,0.2662889144\H,-1.3369851357,-0.7977524494,-0.4075513171\N,-1.3941544249,3.5915382363,0.0227637914\H,-1.0999970003,4.5524496892,0.11428781\O,1.3389475285,-1.1764642688,-0.201493743\O,2.7862300028,1.0908172227,0.1734573682\C,-2.7294426873,1.8010430806,-0.2841022327\C,-2.6966737379,3.1690820114,-0.1485761706\H,-3.5063106981,3.8880566724,-0.165245042\C,-3.9406717543,0.9438261038,-0.4689226171\H,-4.8009118875,1.5698991909,-0.7311623362\H,-3.7876677763,0.2474702256,-1.3027986519\C,-4.2863098129,0.1315197254,0.7815252598\H,-3.4408826988,-0.4901261622,1.0815815538\H,-4.5086448864,0.8049015356,1.6127019355\N,-5.43917354,-0.7346145924,0.600957485\H,-6.3543434039,-0.3258906962,0.727540538\C,-5.3777729664,-1.9952573203,0.1306329967\C,-6.6872865988,-2.7088406761,-0.0475427709\H,-6.7878164461,-3.0081366144,-1.0945623523\H,-6.6788904223,-3.622415308,0.5537932287\H,-7.5525139674,-2.1054429406,0.234261716\O,-4.2977401294,-2.5594951762,-0.1301921057\C,0.6212145106,-2.3763440202,-0.4232921947\H,-0.0911991296,-2.5705128757,0.3865522907\H,0.087110435,-2.3507164571,-1.3797813895\H,1.366986971,-3.1722851222,-0.4463132142\Cu,3.9304127325,-0.455357034,0.1492156302\O,7.731958671,-0.5135836852,0.3074899763\H,7.4842832502,0.398045965,0.0914490664\H,8.286160668,-0.7853939047,-0.4393448193\O,5.3211976756,-1.8727470856,0.158034329\H,5.2969951705,-2.3431162358,-0.6888556057\H,6.2024445278,-1.4283444195,0.172514815\\

Cu(I), NAS, DCM-O1

\\C,-2.531367,2.412828,0.253466\C,
-3.888814,2.77439,0.392403\C,-4.890205,1.820497,0.275362\C,-4.512826,0
.499468,0.016184\C,-3.153641,0.124063,-0.124299\C,-2.149223,1.10433,-0
.001831\H,-5.935539,2.09738,0.381631\H,-1.095818,0.848578,-0.100726\N,
-5.271332,-0.636229,-0.150007\H,-6.279039,-0.681709,-0.114908\O,-1.610
311,3.432255,0.391211\C,-3.124377,-1.288726,-0.385533\C,-4.438225,-1.6
99469,-0.388512\H,-4.85031,-2.688133,-0.549685\C,-1.908017,-2.133558,-
0.589589\H,-2.19346,-3.098868,-1.02025\H,-1.233825,-1.650216,-1.306294
\C,-1.144059,-2.372455,0.715163\H,-0.944193,-1.426095,1.220726\H,-1.73
95,-2.988976,1.391471\N,0.127364,-3.05349,0.519914\H,0.138635,-4.06233
,0.573281\C,1.266069,-2.436128,0.190074\C,2.488766,-3.275355,0.000543\
H,2.878052,-3.116614,-1.008826\H,3.256582,-2.943085,0.704783\H,2.30266
9,-4.340032,0.150288\O,1.297885,-1.1858,0.060171\Cu,2.871881,-0.084221
, -0.321035\O,6.42399,0.565126,1.084979\H,6.512407,-0.399363,1.1043\H,7
.257661,0.866497,0.694133\O,3.503382,3.711346,-0.327348\H,3.521955,4.1
56903,-1.187446\H,2.558226,3.622996,-0.132789\O,4.39863,1.105943,-0.75
4336\H,5.120186,0.94178,-0.105098\H,4.110708,2.034431,-0.59534\H,-4.13
7913,3.81217,0.594655\H,-0.717343,3.074845,0.268759\\

Cu(I), NAS, CDCM-O2

\\C,-0.6849528311,0.2078708036,-0.2501853517\C,-1.354654614
2,1.4715189778,-0.3093478617\C,-0.6907693968,2.677030718,-0.1305810911
\C,0.6862532783,2.6428205497,0.1177148315\C,1.3905743787,1.4173503676,
0.1845327084\C,0.6998570254,0.2033571085,-0.0054672838\H,-1.2292139466
,3.6225156535,-0.1761123238\H,1.2252397123,-0.7487855837,0.0425331949\
N,1.5882860362,3.6597273546,0.3556738876\H,1.3723929409,4.6447850747,0
.385681151\O,-1.341660052,-0.9345631679,-0.4307564669\C,2.7649653952,1
.7381126575,0.4792529346\C,2.8261454736,3.1115793435,0.5734796308\H,3.
6741081375,3.74963422,0.7926251125\C,3.8917965262,0.7726454338,0.66776
28238\H,4.7357677724,1.2792140705,1.1483716985\H,3.5815257478,-0.03426
48788,1.3431532634\C,4.3752222614,0.1421341715,-0.6409835579\H,3.54297
10559,-0.3213446454,-1.1742931544\H,4.7981470942,0.9082876488,-1.29544
4311\N,5.3991998603,-0.8700534728,-0.439987543\H,6.3609043955,-0.56369
762,-0.4002988989\C,5.1393012018,-2.1650277595,-0.1723140392\C,6.32443
30515,-3.0530435569,0.0771095019\H,6.2290158625,-3.4947228984,1.073019
3392\H,6.3117845159,-3.8722756334,-0.6468336085\H,7.2812392686,-2.5328
593031,0.0090564773\O,3.9802071264,-2.6237240194,-0.1440009072\Cu,-3.2
350002801,-1.1115875867,-0.2403472356\O,-5.7755175359,-0.8944320652,2.
656616864\H,-4.9166889565,-0.9501283395,3.1018550591\O,-5.1718899922,-
1.3848386806,-0.0206503938\H,-5.6385159149,-0.7039329429,-0.5601523202
\O,-6.4118133863,0.5240370913,-1.6330154041\H,-7.0158986594,0.04447116
67,-2.2188155991\H,-6.2465047218,-1.6826115167,2.9661176756\H,-5.69911
44806,0.8123662222,-2.2227278319\H,-5.4115387438,-1.1849069546,0.91417
81642\H,-2.4259656066,1.4685799918,-0.4984081336\\