Electronic Supplementary Information (ESI)

One-Pot Synthesis, Characterisation and Kinetic Stability of Novel Side-Bridged Pentaazamacrocyclic Copper(II) Complexes

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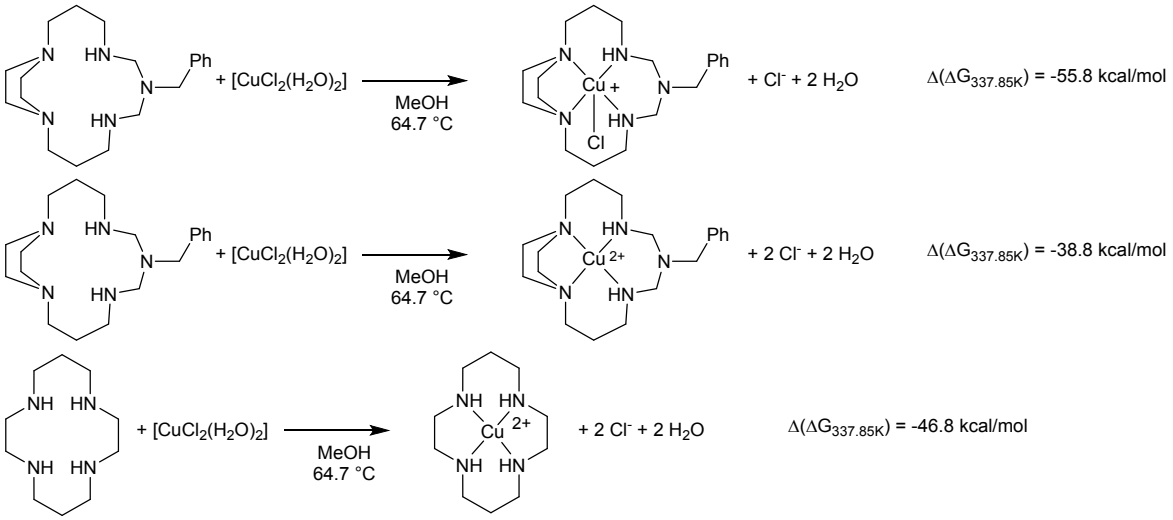
Computed free enthalpies of formation of complexes 7-Benzyl-1,5,7,9,13-penta-aza-(1,13-ethano)-cyclopentadecane copper(II) dichloride and copper(II) cyclam dichloride



Thermodynamics of the coordination reactions between copper(II) chloride dihydrate and ligands 7-Benzyl-1,5,7,9,13-penta-aza-(1,13-ethano)-cyclopentadecane or 1,4,8,11-Tetraazacyclotetradecane (cyclam) were examined using DFT calculations. Full coordinates for all stationary points, together with computed free Gibbs energy and vibrational frequency data, are also available via the corresponding Gaussian 09 output files, stored in the digital repository (DOI: 10.6084/m9.figshare.907517):
http://figshare.com/articles/One_Pot_Synthesis_Characterisation_and_Kinetic_Stability_of_Novel_Side_Bridged_Pentaazamacrocylic_Copper_II_Complexes_/907517
or
http://dx.doi.org/10.6084/m9.figshare.907517

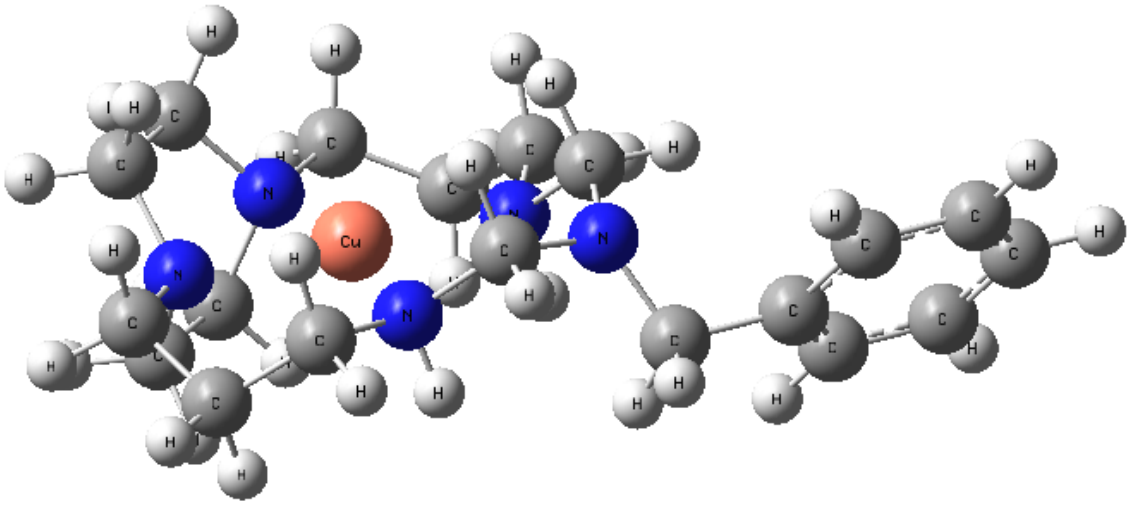
Table S1. Thermodynamic data evaluations

System	*G (Hartree)*	*$\Delta(\Delta G_{337.85K})$ (kcal mol^{-1})*
$[CuCl_2(H_2O)_2]$	-2713.526338	-
H_2O	-76.405277	-
Cl^-	-460.362767	-
7-Benzyl-1,5,7,9,13-penta-aza-(1,13-ethano)-cyclopentadecane	-1016.470419	-
1,4,8,11-Tetraazacyclotetradecane (cyclam)	-613.787527	-
7-Benzyl-1,5,7,9,13-penta-aza-(1,13-ethano)-cyclopentadecane + $[CuCl_2(H_2O)_2]$	-3729.996757	0.0
7-Benzyl-1,5,7,9,13-penta-aza-(1,13-ethano)-cyclopentadecane copper(II) chloride *(+ $2H_2O$ + Cl^-)*	-3116.912393 *(-2*76.405277 –460.362767=-3730.085714)*	-55.8
7-Benzyl-1,5,7,9,13-penta-aza-(1,13-ethano)-cyclopentadecane copper(II) *(+ $2H_2O$ + $2Cl^-$)*	-2656.522535 *(-2*76.405277 –2*460.362767=-3730.058623)*	-38.8
cyclam + $[CuCl_2(H_2O)_2]$	-3327.313865	0.0
copper(II) cyclam dichloride *(+ $2H_2O$ + $2Cl^-$)*	-2253.852408 *(-2*76.405277 –2*460.362767=-3327.388496)*	-46.8

Optimized geometries and computed free energies

Full coordinates for all the stationary points, together with their 3 lowest calculated vibrations and their computed Free Gibbs Energy are reported below.

7-Benzyl-1,5,7,9,13-penta-aza-(1,13-ethano)-cyclopentadecane copper(II)



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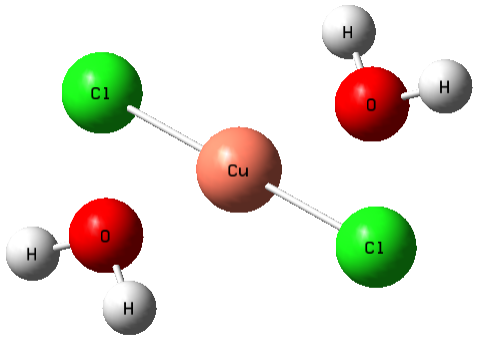
C	5.23249063	0.98001200	3.19799492
C	4.38589442	1.30800553	4.40928899
C	5.01693287	2.36616134	5.28901332
C	5.59069139	4.70268731	5.64825968
N	5.23006079	6.06329861	5.44263907
C	5.67404522	6.64013068	4.22218743
C	5.37181717	6.93409062	1.83109726
C	4.78697248	6.44463270	0.52246776
C	5.56857579	5.28994248	-0.06449316
C	4.24546136	3.28061525	0.36584406
C	4.13007344	2.07776981	1.31045969
C	6.52731606	1.94730584	1.38196677
C	6.64477599	3.18464877	0.49227383
C	3.90692749	6.48002962	5.92365733
Cu	5.26261163	4.06761543	2.78828396
H	6.25628886	0.76693271	3.52803146
H	4.86358175	0.07939891	2.68483648
H	4.28316730	0.38941471	4.99762622
H	3.36324832	1.59849038	4.12906228
H	6.09472963	2.18272121	5.39497404
H	4.58133986	2.33744135	6.29779448
H	6.66088388	4.56252713	5.45295477
H	5.39471711	4.42419778	6.69344334
H	5.49822952	7.72468102	4.24781407
H	6.75067170	6.46929308	4.09493763
H	5.03655983	7.95933583	2.03915013
H	6.46856468	6.95716227	1.77403637

H	4.82223749	7.26803988	-0.19946113
H	3.72223770	6.19727361	0.64151564
H	6.62975221	5.56309817	-0.10704509
H	5.24851688	5.07213887	-1.09430655
H	3.37734225	3.94105159	0.45543920
H	4.32421401	2.96725875	-0.68536834
H	3.22160798	2.13461576	1.91833380
H	4.10525389	1.12715991	0.75799710
H	7.38780910	1.86641958	2.05216256
H	6.46341281	1.01744062	0.79743237
H	7.53796044	3.76516240	0.74308107
H	6.69620710	2.92555765	-0.57556845
H	3.82946217	7.55790242	5.72700625
H	3.07688393	6.00435733	5.36965740
C	3.72980452	6.20725359	7.39196655
C	2.76437267	5.30398458	7.83671593
C	4.54155465	6.85330276	8.32922158
C	2.60530335	5.04953562	9.19881788
H	2.12886082	4.79555316	7.11121699
C	4.38473913	6.60291872	9.68799004
H	5.29869162	7.55633364	7.98398149
C	3.41524843	5.69916471	10.12559112
H	1.85034827	4.34237625	9.53366573
H	5.01670390	7.11553244	10.40939359
H	3.29336736	5.50465456	11.18843632
N	5.00872778	6.08673285	2.99283541
H	3.99680350	6.18758707	3.11772859
N	4.85308606	3.74206065	4.76052488
H	3.85501935	3.96194598	4.83591824

Sum of electronic and thermal Free Energies= -2656.522535
Frequencies -- 24.1613 35.1103 49.0799

Copper(II) chloride dihydrate



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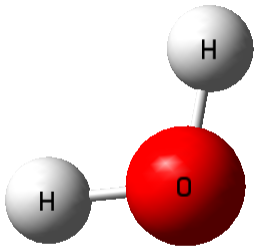
Cu	-0.00009700	0.00018700	0.00007900
Cl	-2.22632500	-0.00133000	-0.00015300
Cl	2.22622100	0.00087000	-0.00012900
O	0.00210600	-1.99609500	0.09330800
H	0.78830900	-2.39371900	-0.30994200
H	-0.78206700	-2.39666100	-0.31106100
O	-0.00188000	1.99632000	-0.09306100
H	0.78343600	2.39632100	0.30964200
H	-0.78690400	2.39464700	0.31187200

Sum of electronic and thermal Free Energies= -2713.526338

Frequencies -- 33.2317 131.9846 138.0293

Water



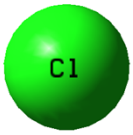
0 1

O	0.00000000	0.00000000	0.11739500
H	0.00000000	0.76400300	-0.46958000
H	0.00000000	-0.76400300	-0.46958000

Sum of electronic and thermal Free Energies= -76.405277

Frequencies -- 1589.7778 3861.0428 3980.0074

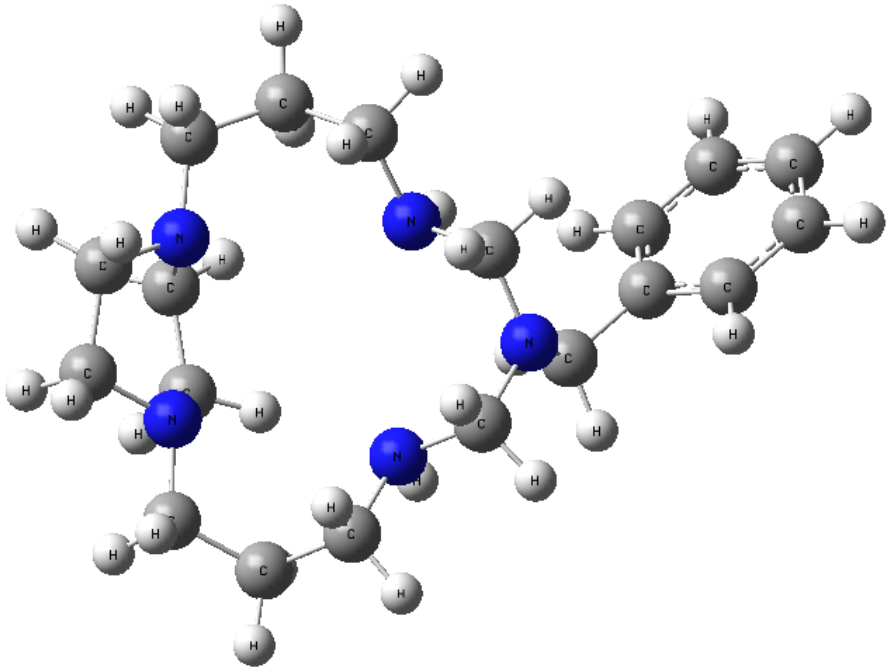
Chloride



-1 1
Cl 0.00000000 0.00000000 0.00000000
Sum of electronic and thermal Free Energies= -460.362767

Frequencies -- None

7-Benzyl-1,5,7,9,13-penta-aza-(1,13-ethano)-cyclopentadecane



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N	2.95407449	0.04580756	2.78228379
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C	2.82625869	0.10737741	4.22285652
C	1.45717323	-0.30589686	4.75343293
C	0.29061077	0.51916102	4.21350711
C	-1.40132758	0.76604395	2.51062952
N	-1.96372943	0.37859953	1.23967523
C	-1.27036100	0.76989936	0.03839088
C	0.57420467	0.49749065	-1.50203124
C	1.78384311	-0.33865817	-1.91456346
C	3.10522203	0.04231028	-1.25312813
C	2.81056970	-1.28867748	0.74022107
C	3.03085965	-1.30363392	2.25909388
C	4.08553010	0.81287080	2.28858883
C	4.30030476	0.55207933	0.78747197
C	-2.58336106	-0.93638294	1.19138545
H	3.00830374	1.15198023	4.52051881
H	3.61703367	-0.49808175	4.72123011
H	1.49677871	-0.20672929	5.84662300
H	1.26669599	-1.37278550	4.56332487
H	0.65699962	1.51807201	3.92689025
H	-0.45352707	0.68463628	5.01828560
H	-0.98976445	1.77888950	2.39589857
H	-2.23399871	0.84195384	3.24015272
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H	-0.91571484	1.80308627	0.16901017
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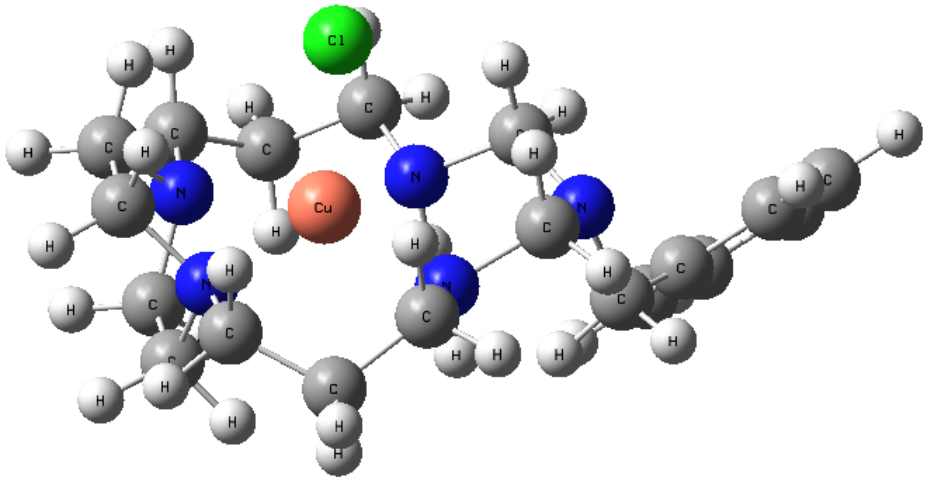
H	0.90215196	1.52107607	-1.25892894
H	1.93610066	-0.23184255	-2.99682753
H	1.56087699	-1.40454815	-1.75647635

H	3.37254749	1.06125156	-1.57274711
H	3.90231000	-0.63167712	-1.64375827
H	1.77215904	-1.55102210	0.50822583
H	3.46742582	-2.04884261	0.26274361
H	2.26492535	-1.92638499	2.73467115
H	4.01489684	-1.75812176	2.51282087
H	3.88758356	1.87748514	2.47670609
H	5.01570625	0.55089832	2.83914903
H	4.58090973	1.48310223	0.27958451
H	5.14489239	-0.15616981	0.63455083
H	-2.98197445	-1.06361179	0.17250427
H	-1.85876177	-1.75989263	1.34345947
C	-3.70807544	-1.08164819	2.18455140
C	-3.66908193	-2.05659060	3.18097588
C	-4.81754367	-0.23274853	2.11527004
C	-4.71422307	-2.18340317	4.09713893
H	-2.81051011	-2.72559913	3.24219681
C	-5.86289048	-0.35593413	3.02394746
H	-4.85017455	0.53196750	1.33991288
C	-5.81262674	-1.33234780	4.02067754
H	-4.66635434	-2.94601495	4.87114379
H	-6.72152263	0.30849678	2.95583864
H	-6.62882497	-1.42704682	4.73318057
N	-0.32788746	-0.07716230	3.03294997
H	-0.70900904	-0.98521474	3.29707934
N	-0.11283066	-0.03844359	-0.33160811
H	-0.42469815	-0.98550459	-0.54663148

Sum of electronic and thermal Free Energies= -1016.470419

Frequencies -- 28.8244 35.2271 49.0897

7-Benzyl-1,5,7,9,13-penta-aza-(1,13-ethano)-cyclopentadecane copper(II) dichloride



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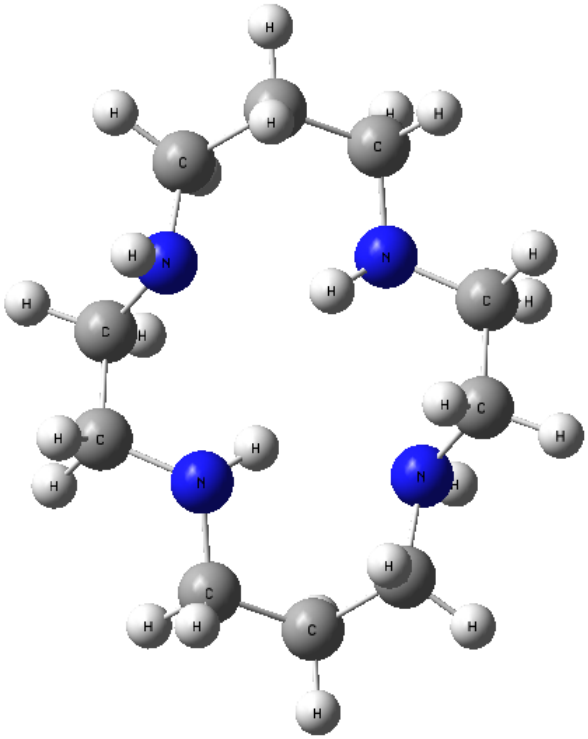
Cl	8.06642455	4.18454185	3.06493651
N	5.30679071	2.09562635	2.27879361
N	5.39545443	4.03549507	0.75329691
C	5.31962031	1.01085150	3.27700851
C	4.65212099	1.36154782	4.58941625
C	5.37097896	2.44937816	5.36104028
C	5.76056991	4.82082351	5.70675653
N	5.32901050	6.15754603	5.45423920
C	5.79705260	6.73434563	4.23631491
C	5.60488939	6.92959215	1.82700374
C	4.90921921	6.49184898	0.55424789
C	5.51640833	5.25299935	-0.06910595
C	4.03792281	3.44949103	0.68433390
C	3.99564079	2.22007871	1.60483153
C	6.32945214	1.83413503	1.24633844
C	6.35591734	3.01713815	0.28113674
C	3.94495500	6.48020724	5.81659950
Cu	5.64427558	4.09652585	2.84441413
H	6.37229978	0.76694570	3.47079285
H	4.85762023	0.11593647	2.82924133
H	4.64846004	0.45297133	5.20263792
H	3.59412393	1.62818090	4.45214389
H	6.45801017	2.28745304	5.34173471
H	5.05573612	2.42908411	6.41548776
H	6.84089239	4.74164240	5.53635356
H	5.54703898	4.55971780	6.75368255
H	5.56640145	7.81019724	4.23816479
H	6.88351541	6.60684461	4.15516175
H	5.37609615	7.98623040	2.02995251
H	6.69589533	6.84511104	1.72345462
H	5.00043279	7.29938646	-0.18135345
H	3.83012133	6.37543746	0.72966362
H	6.58844071	5.42812651	-0.22596239
H	5.07319483	5.05465586	-1.05848849
H	3.30871407	4.20237754	1.00010939
H	3.81164743	3.18185171	-0.35973976

H	3.21311558	2.32464251	2.36266944
H	3.79210337	1.29666529	1.04014166
H	7.29473581	1.73088240	1.75113625
H	6.09525750	0.88681611	0.73599631
H	7.35042442	3.47207269	0.26490103
H	6.08948217	2.72328651	-0.74625749
H	3.82157831	7.55944992	5.64939402
H	3.19948044	5.98162753	5.16834968
C	3.63930877	6.14214464	7.24974669
C	2.68369141	5.17621183	7.56543951
C	4.32207726	6.78669447	8.28566781
C	2.40661954	4.85866591	8.89513651
H	2.14655502	4.66847747	6.76393725
C	4.04977638	6.47167621	9.61246877
H	5.07264500	7.53756598	8.04212688
C	3.09010289	5.50608111	9.92020858
H	1.65869542	4.10450524	9.12795051
H	4.58375536	6.98229277	10.41046925
H	2.87715603	5.26145264	10.95809200
N	5.20929103	6.12696085	3.00370425
H	4.19137982	6.19941813	3.08252444
N	5.11510140	3.80182811	4.82418620
H	4.10329731	3.94982119	4.87184339

Sum of electronic and thermal Free Energies= -3116.912393

Frequencies -- 21.3573 34.8435 47.2832

Cyclam



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N	-0.20991600	2.02692800	0.82283400
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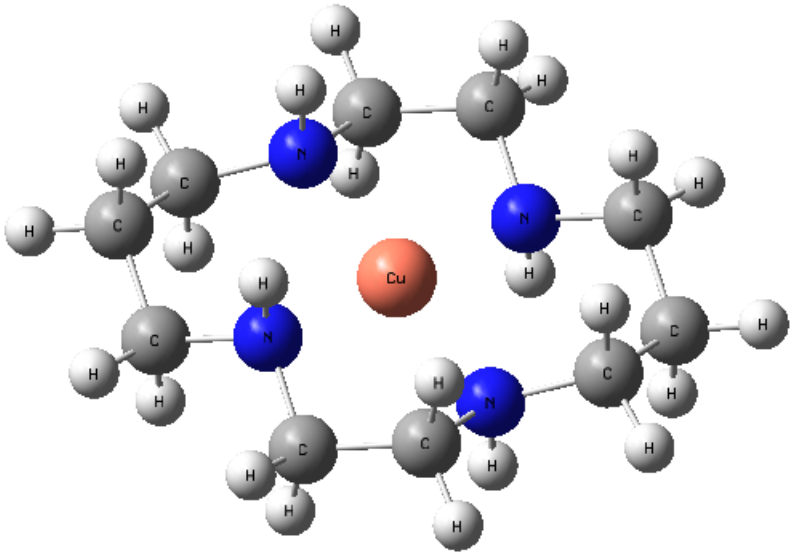
C	1.11897100	1.84948400	1.38208200
C	1.20026000	0.65241000	2.31114000
C	1.37693300	-1.80194200	2.15264500
C	1.53360800	-2.86717100	1.07184300
C	-0.29591500	3.06346300	-0.20312200
H	-0.87636700	2.22271800	1.56747000
H	0.87026900	-0.51549200	0.63076900
H	1.80752700	1.68195300	0.53753900
H	1.48794200	2.74755100	1.91510500
H	2.24197400	0.59271600	2.68432500
H	0.57120800	0.83044300	3.20199400
H	2.36997600	-1.62152300	2.60967800
H	0.74190600	-2.20475300	2.96221400
H	2.37959100	-2.60825000	0.41587500
H	1.79924200	-3.81430700	1.55965300
H	-0.28345500	4.08011500	0.23084800
H	0.60434700	2.98580700	-0.83191300
N	0.20991600	-2.02692800	-0.82283400
N	-0.80041500	0.56936300	-1.64568400
C	0.29591500	-3.06346300	0.20312200
C	-1.53360800	2.86717100	-1.07184300
C	-1.11897100	-1.84948400	-1.38208200
H	0.87636700	-2.22271800	-1.56747000
C	-1.20026000	-0.65241000	-2.31114000
C	-1.37693300	1.80194200	-2.15264500
H	-0.87026900	0.51549200	-0.63076900
H	0.28345500	-4.08011500	-0.23084800

H	-0.60434700	-2.98580700	0.83191300
H	-2.37959100	2.60825000	-0.41587500
H	-1.79924200	3.81430700	-1.55965300
H	-1.80752700	-1.68195300	-0.53753900
H	-1.48794200	-2.74755100	-1.91510500
H	-2.24197400	-0.59271600	-2.68432500
H	-0.57120800	-0.83044300	-3.20199400
H	-2.36997600	1.62152300	-2.60967800
H	-0.74190600	2.20475300	-2.96221400

Sum of electronic and thermal Free Energies= -613.787527

Frequencies -- 22.4749 45.3751 72.1406

copper(II) cyclam dichloride



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Cu	0.00000000	0.00000000	0.00000000
N	-0.01562900	1.88522700	0.75461100
N	1.46471400	-0.36896200	1.35765000
C	1.22130700	2.03360400	1.55380200
C	1.45119000	0.75567700	2.31940700
C	1.41628600	-1.68577000	2.03003100
C	1.44788200	-2.83846300	1.04716400
C	-0.18535800	2.98439800	-0.22167500
H	-0.81353600	1.90827900	1.39630200
H	2.33766200	-0.32084800	0.82470900
H	2.04571300	2.21805900	0.85322800
H	1.15315800	2.89789600	2.22534800
H	2.38524600	0.79293100	2.89286400
H	0.63106200	0.57597300	3.02657500
H	2.26149500	-1.75714700	2.72843400
H	0.49510400	-1.71360000	2.62715600
H	2.32708500	-2.75764800	0.39034300
H	1.58493300	-3.76393900	1.61725800
H	-0.19208700	3.94041900	0.31980400
H	0.70016200	2.98142600	-0.87085700
N	0.01562900	-1.88522700	-0.75461100
N	-1.46471400	0.36896200	-1.35765000
C	0.18535800	-2.98439800	0.22167500
C	-1.44788200	2.83846300	-1.04716400
C	-1.22130700	-2.03360400	-1.55380200
H	0.81353600	-1.90827900	-1.39630200
C	-1.45119000	-0.75567700	-2.31940700
C	-1.41628600	1.68577000	-2.03003100
H	-2.33766200	0.32084800	-0.82470900
H	0.19208700	-3.94041900	-0.31980400
H	-0.70016200	-2.98142600	0.87085700
H	-2.32708500	2.75764800	-0.39034300
H	-1.58493300	3.76393900	-1.61725800
H	-2.04571300	-2.21805900	-0.85322800

H	-1.15315800	-2.89789600	-2.22534800
H	-2.38524600	-0.79293100	-2.89286400
H	-0.63106200	-0.57597300	-3.02657500
H	-2.26149500	1.75714700	-2.72843400
H	-0.49510400	1.71360000	-2.62715600

Sum of electronic and thermal Free Energies= -2253.852408

Frequencies -- 37.9422 88.9160 117.5807

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