Electronic Supplementary Material (ESI) for Dalton Transactions.

Electrocatalytic Hydrogen Evolution by a Dinuclear Copper Complex and Mechanistic Elucidation through DFT Studies

Manaswini Raj,[a] *Koushik Makhal,* [b] *Dev Raj,* [a] *Aman Mishra,* [a] *Bhabani S. Mallik,*[b] *and Sumanta Kumar Padhi* [a,*]

[a] Artificial Photosynthesis Laboratory, Department of Chemistry and Chemical Biology, Indian Institute of Technology (Indian School of Mines), Dhanbad, 826004, India.

[b] Department of Chemistry, Indian Institute of Technology Hyderabad, Sangareddy, 502284, Telangana, India.

*Email: sumanta@iitism.ac.in

SUPPORTING INFORMATION

Material and methods

Materials

All the reagent-grade chemicals utilized in this work were purchased and utilized as delivered. The commercially available analytical-grade solvents employed were bought and used after their purification before any use. HPLC grade solvents were procured, and their usage has been made for various analytical and electrochemical studies.

Optical measurements

UV-Vis studies conducted throughout the work were recorded on Agilent Technologies Cary 8454 photodiode array UV–Visible spectrophotometer.

Mass spectra

The Q-Tof-Premier-ESI-MS instrument performed high-resolution ESI mass spectra.

EPR Spectroscopy. X-band EPR spectra were recorded at 120 K using a Bruker EMX 1444 EPR spectrometer operating at 9.442 GHz. Spectra were treated using the Bruker WINEPR software and simulated using the Bruker SIMFONIA software.

Single-crystal X-ray crystallography

Rigaku SuperNova G8910B EosS2 single-crystal X-ray diffractometer equipped with an EosS2 CCD detector and having Mo Kα radiation (λ = 0.71073 Å) was used to collect the X-ray diffraction data out of suitable [$\mathbf{Cu^{II}_2(L^1)_2}$] single-crystals at 293 K. CrysAlis^{Pro} software was utilized for the data integration purpose. The software was also used to determine the single-crystal unit cell. Further Olex2 software associated with the Charge Flipping solution program was used to solve the crystals' structure. Gauss-Newton minimization of the Olex2 refinement package was operated for the data refinement of the structure of the crystals.

Electrochemistry

The electrochemical responses were recorded using ALS/CHI model 1140C electrochemical analyser. All the electrochemical investigations were performed using 0.1 M tetrabutylammonium perchlorate ($^nBu_4NClO_4$, TBAP) as a supporting electrolyte in 95/5 (v/v) DMF/H_2O solution under an inert atmosphere in a three-electrode configuration. The three-electrode system includes a glassy carbon rod (A= 0.07 cm^2) as a working electrode, platinum wire as a reference electrode, and saturated calomel electrode as reference electrodes, respectively. The catalytic ability of electrocatalyst towards electrocatalytic hydrogen evolution reaction was studied at varying complex concentrations (0.50 mM, 0.75 mM, and 1.0 mM) with the addition of acetic acid as the external H^+ source. CH instrument model 660D electrochemical analyser was used to record the Electrochemical Impedance Spectroscopy (EIS).

Controlled potential coulometry

The controlled potential coulometry for the analyte was conducted in a custom-made air-tight electrolytic cell. Glassy carbon rods as working electrodes, platinum mesh as counter electrodes, and saturated calomel electrodes as reference electrodes were used for experiments. For the electrolysis purpose, 0.05 mM of analyte was examined in 95/5 (v/v) DMF/H_2O medium by addition of 30 equivalent of acetic acid as a proton source and using 0.1 M $^nBu_4NClO_4$ as supporting electrolyte. The electrolysis was conducted under inert conditions for half an hour at room temperature.

Hydrogen evolution studies

GC-2011 (CIC India limited), equipped with a TCD detector, was used for the GC analysis using Ar as the carrier gas. The released gaseous sample was collected after the completion of the controlled potential electrolysis at the headspace aliquots of the customized-electrolytic cell by the use of a Hamilton gas-tight syringe, followed by its injection in the instrument for further detection and analysis purposes.

Spectro-electrochemistry

The UV-Vis Spectro electrochemical investigation was monitored by simultaneously recording optical and electrochemical changes using 8454 UV-Vis spectrophotometer and CHI 1140, respectively. The Quartz cuvette holding 0.05 mM analyte solution with the addition of 30 equiv. of acetic acid as the external acid source was employed. The electrolysis was carried out under an inert atmosphere for half an hour using Pt mesh as the working electrode, Pt wire as the counter electrode, and Ag wire reference electrodes, respectively.

FESEM and EDX studies

Supra 55 (Carl Zeiss, Germany) field-emission scanning electron microscopy (FESEM) system was used for recording the data for the surface morphology of the working electrode.

XPS studies

After the controlled-potential coulometry, the XPS analysis of the compound was recorded using PHI 5000 versa probe III equipped with a monochromatic argon ion gun with AI as the source and compucentric Zalar™ rotation.

Synthesis of $[Cu^{II}_2(L^1)_2]$ (Cu 1)

A solution of one equivalent of ligand **L^1** (2-{[2-(8-hydroxyquinolin-2-yl)-1*H*-benzimidazol-1-yl]methyl}quinolin-8-ol), (0.1 g, 0.23 mmol) and one equivalent of $Cu(CH_3COO)_2.H_2O$ (0.047 g, 0.23 mmol) in a mixture of DCM and CH_3OH solvent was stirred for 4-5 hours at room temperature. The solvent mixture was reduced under vacuum to yield a brown-coloured solid product. The brown-coloured precipitate was washed with ice-cold methanol and excess diethyl ether, followed by drying in vacuo. The slow evaporation of the complex in DMF was carried out to yield brown-coloured crystals suitable for SC-XRD analysis. Yield (56 % concerning Cu metal centre). Calculated mass for $[C_{52}H_{32}Cu_2N_8O_4 + Na^+]$ = 981.10; found value= 981.09. Calculated mass for $[C_{52}H_{32}Cu_2N_8O_4 + H^+]$ = 959.12 and found value= 959.11. Elemental analysis calculated for $C_{52}H_{32}Cu_2N_8O_4$; C, 65.06; H, 3.36; N, 11.67% and found for C, 65.09; H, 3.38; N, 11.69%.

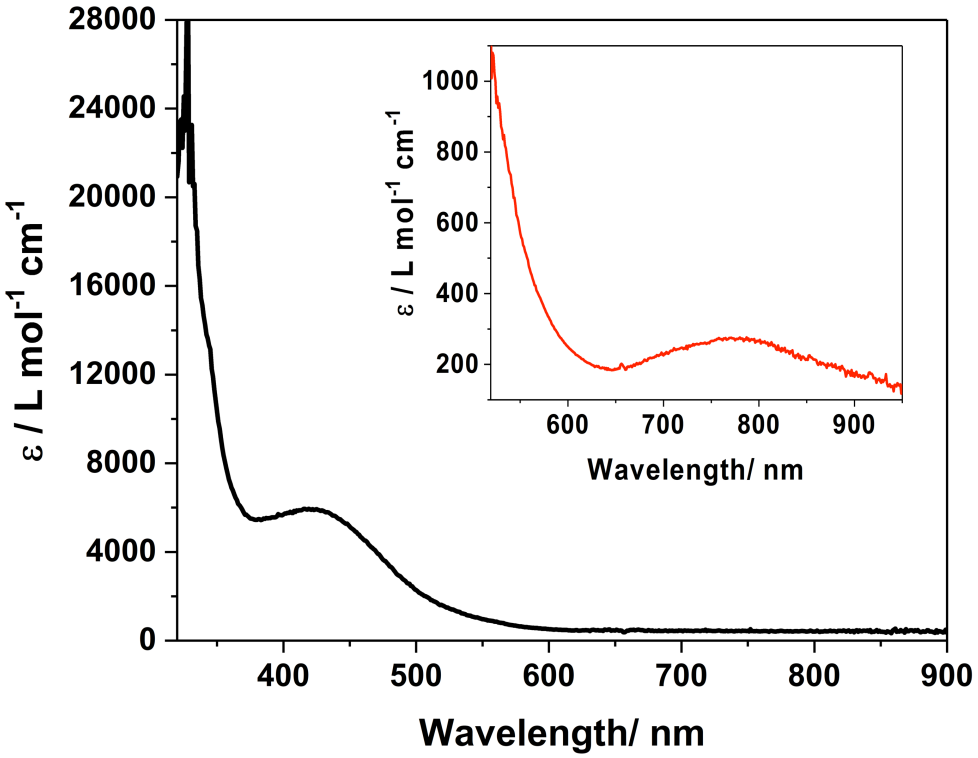


Figure S1. The UV-Vis spectra of [**Cu 1**] (0.125 mM) in DMF (Inset 1.5 mM of [**Cu 1**] in DMF).

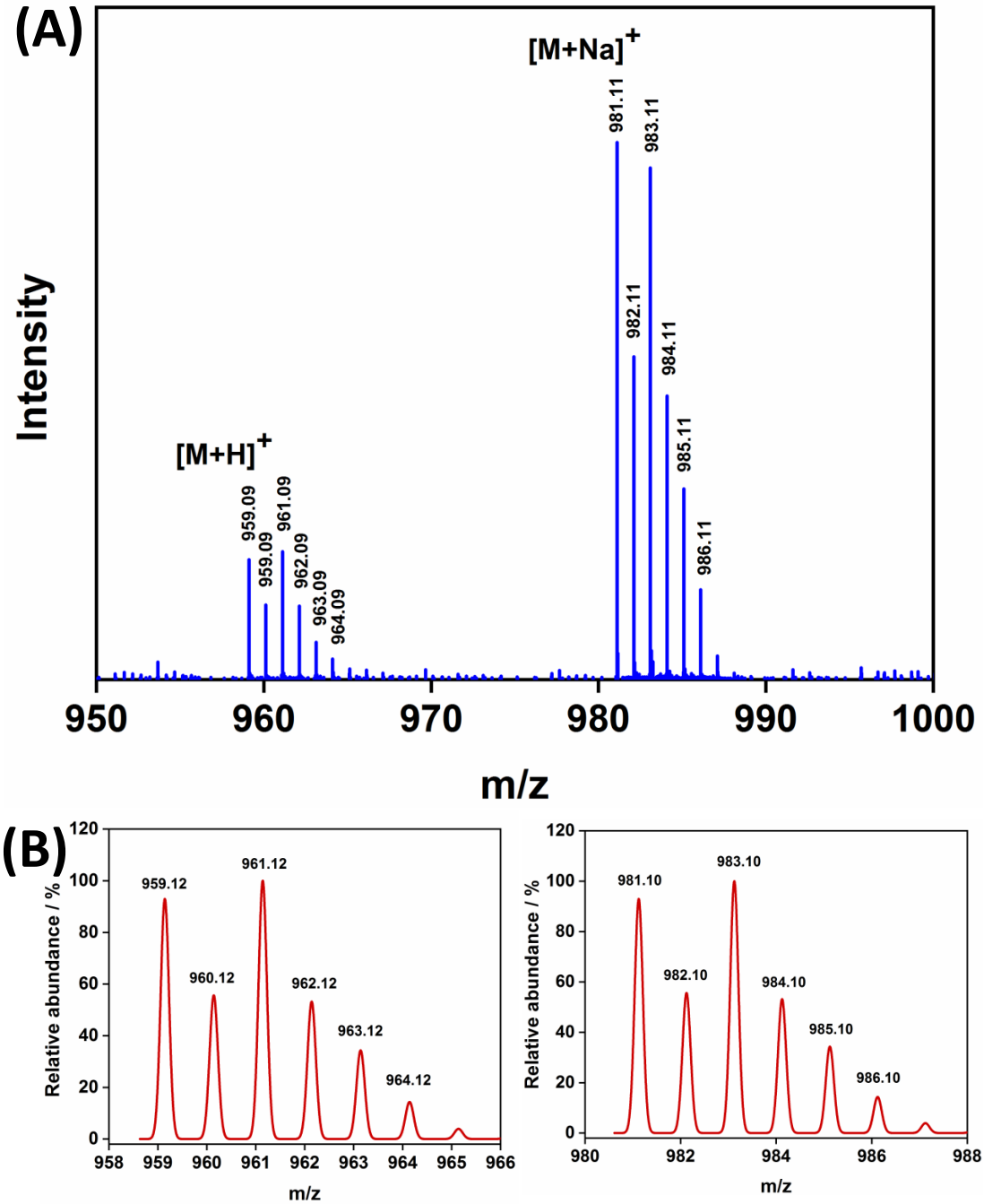


Figure S2. Mass spectra of [**Cu 1**] in DMF.

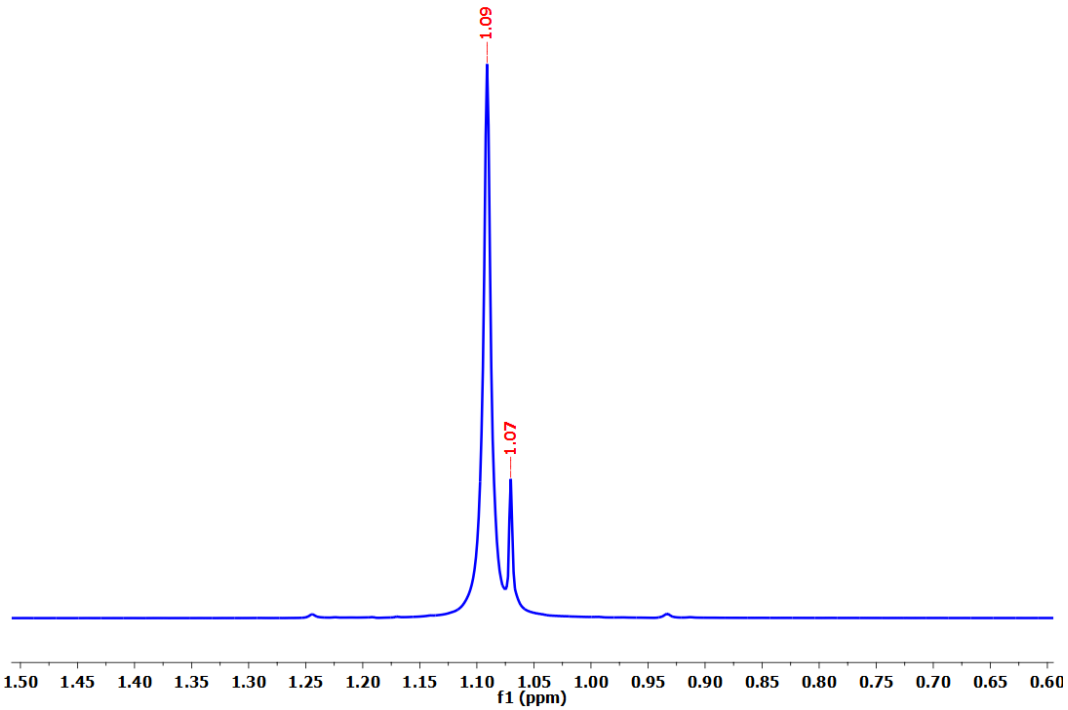


Figure S3. ^{1}H NMR spectra of *t*-BuOH for measurement of magnetic susceptibility of [**Cu 1**] by Evans method in 10 % *t*-BuOH and DMSO mixture at 25°C.

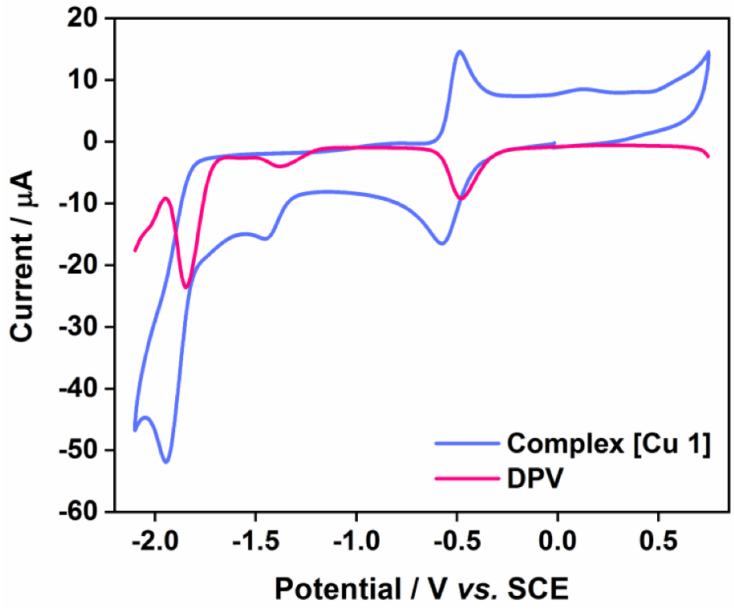


Figure S4. Cyclic voltammogram and DPV of [**Cu 1**]. Electrocatalytic condition: 1.0 mM of the complex in DMF with 0.1 M TBAP as supporting electrolyte.

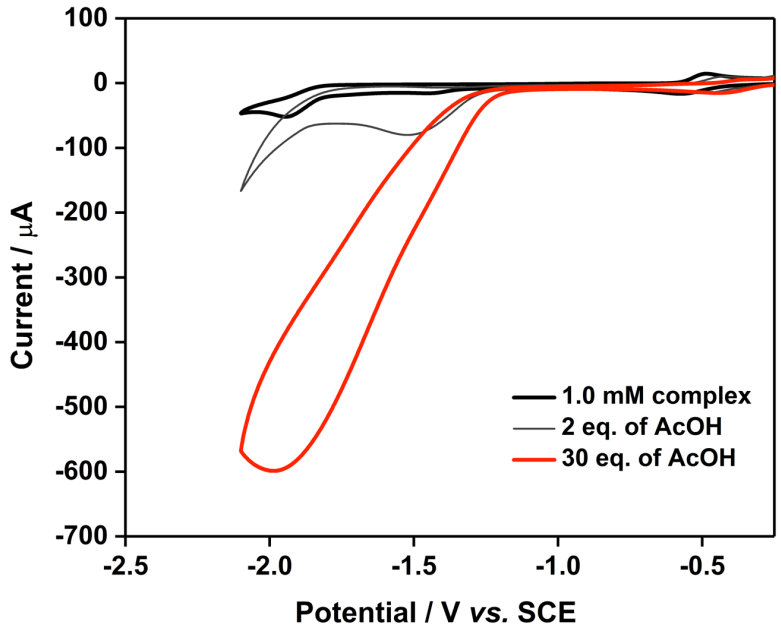


Figure S5. Cyclic voltammogram of [**Cu 1**] and after addition of 2 equivalent of CH_3COOH and 30 equivalent of CH3COOH. Electrocatalytic condition: 1.0 mM of the complex in 95/5 (v/v) DMF/H_2O with 0.1 M TBAP as supporting electrolyte at a scan rate of 100 mV s^{-1} under an inert atmosphere using a three-electrode configuration.

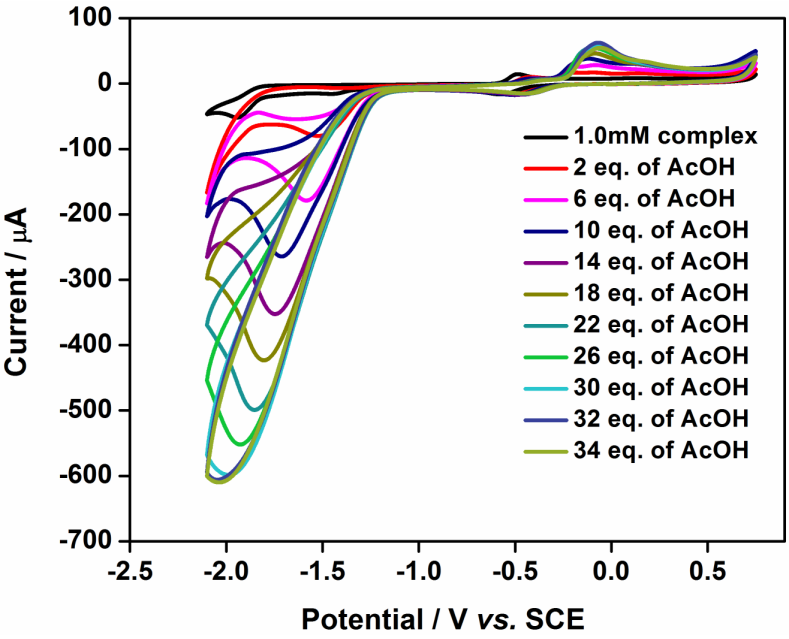


Figure S6. Electrocatalytic proton reduction by 1.0 mM of [**Cu 1**]. Electrocatalytic condition: [**Cu 1**] in 95/5 (v/v) DMF/H_2O in the presence of 0.1 M TBAP as supporting electrolyte at a scan rate of 100 mV s^{-1} under an inert atmosphere using three-electrode configuration.

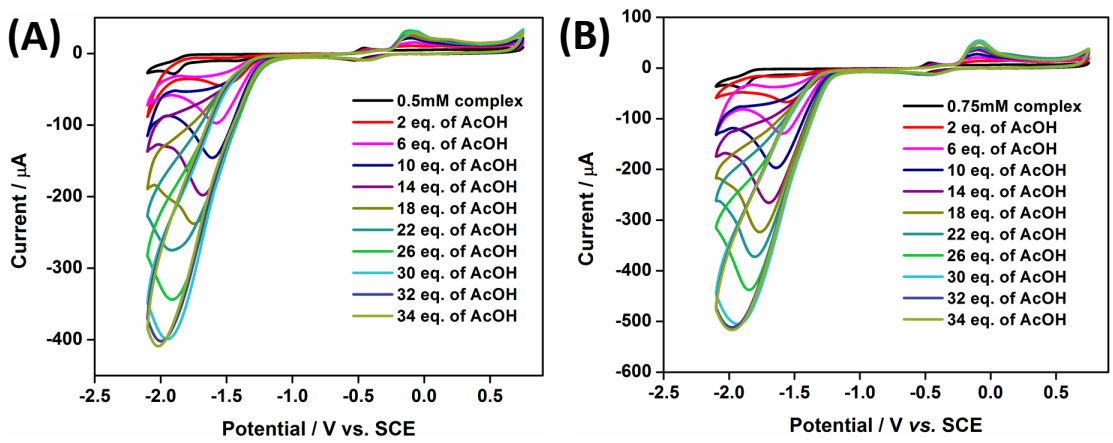


Figure S7. Electrocatalytic proton reduction by (a) 0.5 mM and (b) 0.75 mM of [**Cu 1**]. Electrocatalytic condition: [**Cu 1**] in 95/5 (v/v) DMF/H_2O in presence of 0.1 M TBAP as supporting electrolyte at a scan rate of 100 mV s^{-1} under inert atmosphere using three-electrode configuration.

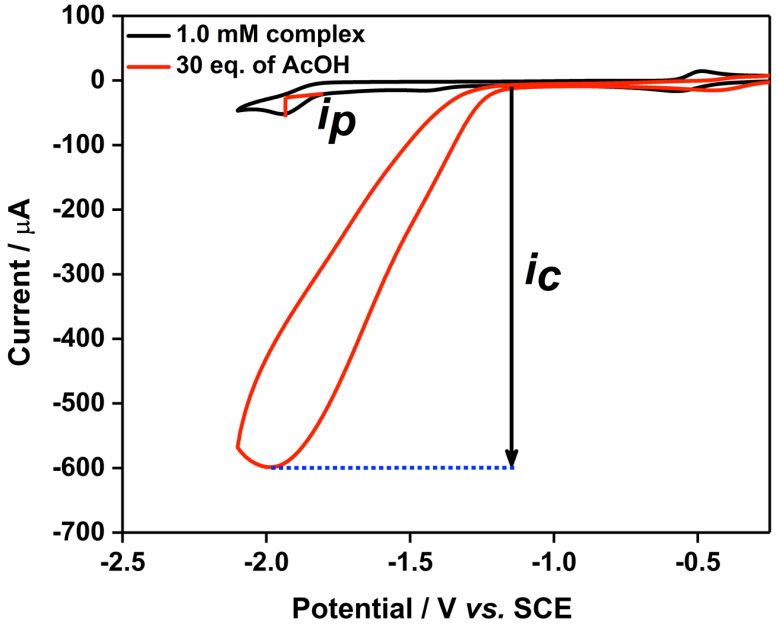


Figure S8. Plot displaying i_c and i_p current for [**Cu 1**]. Electrocatalytic condition: 1.0 mM of [**Cu 1**] in 95/5 (v/v) DMF/H_2O in the presence of 0.1 M TBAP as supporting electrolyte at a scan rate of 100 mV s^{-1} under an inert atmosphere using three-electrode configuration.

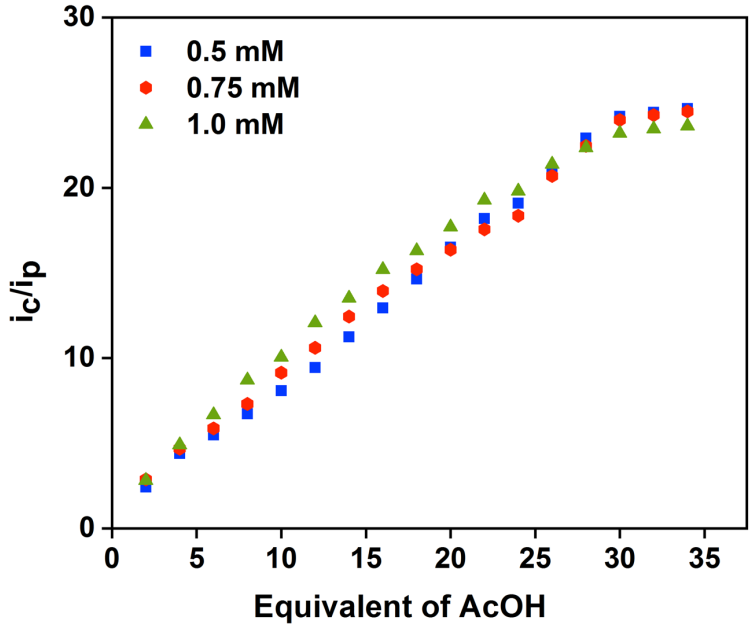


Figure S9. Plot of i_c/i_p *vs.* equivalents of AcOH for three distinct concentrations (0.5 mM, 0.75 mM and 1.0 mM) of [**Cu 1**]. Electrocatalytic condition: [**Cu 1**] in 95/5 (v/v) DMF/H_2O in the presence of 0.1 M TBAP as supporting electrolyte at a scan rate of 100 mV s^{-1} under an inert atmosphere using three-electrode configuration.

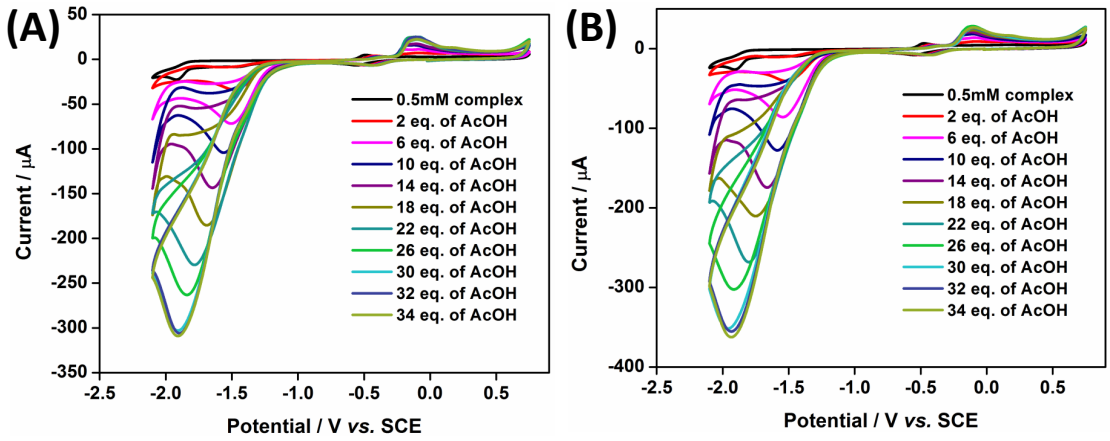


Figure S10. Electrocatalytic proton reduction by [**Cu 1**] at a scan rate of (a) 50 mV s^{-1} and (b) 75 mV s^{-1}. Electrocatalytic condition: 1.0 mM of [**Cu 1**] in 95/5 (v/v) DMF/H_2O in presence of 0.1 M TBAP as supporting electrolyte under inert atmosphere using three-electrode configuration.

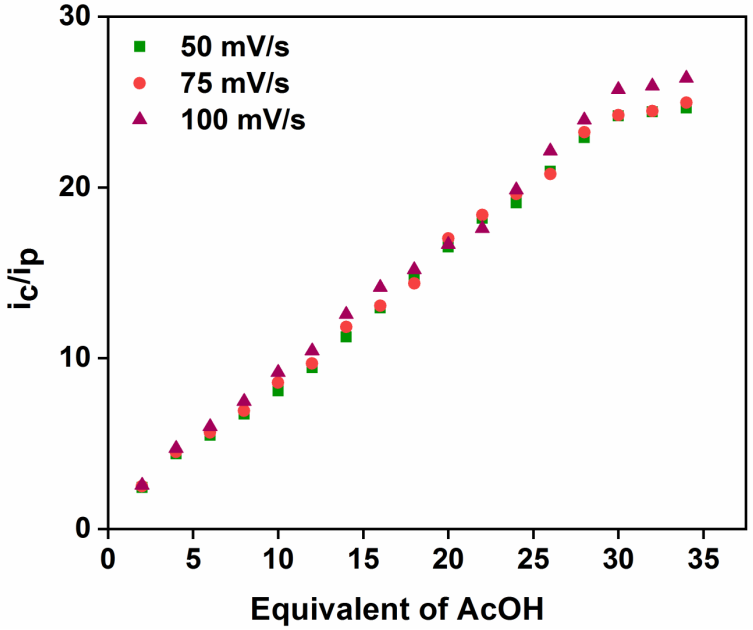


Figure S11. Plot of i_c/i_p *vs.* equivalents of AcOH for three distinct scan rate (50 mV s^{-1}, 75 mV s^{-1} and 100 mV s^{-1}) for [**Cu 1**]. Electrocatalytic condition: 1.0 mM of [**Cu 1**] in 95/5 (v/v) DMF/H_2O in presence of 0.1 M TBAP as supporting electrolyte under inert atmosphere using three-electrode configuration.

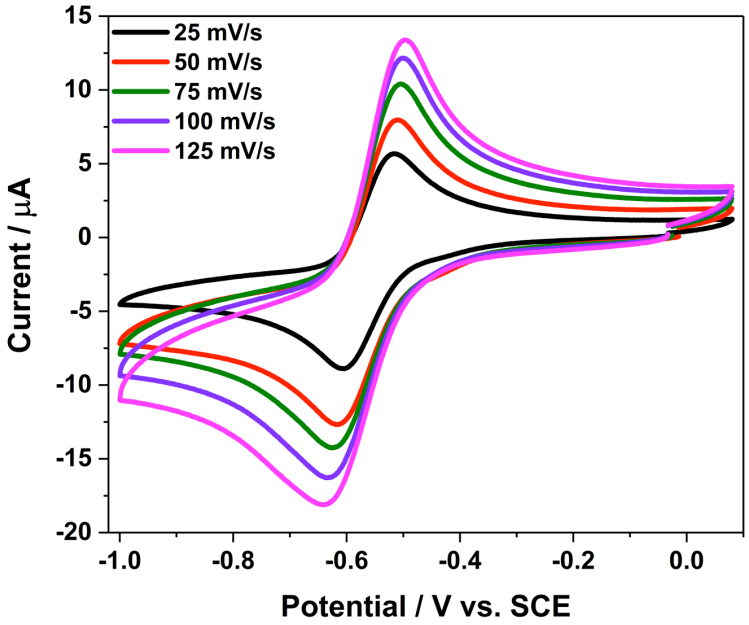


Figure S12. Cyclic voltammograms of 1.0 mM [**Cu 1**] in presence of 0.1 M TBAP in DMF at varying scan rates from 25 to 125 mV s^{-1}.

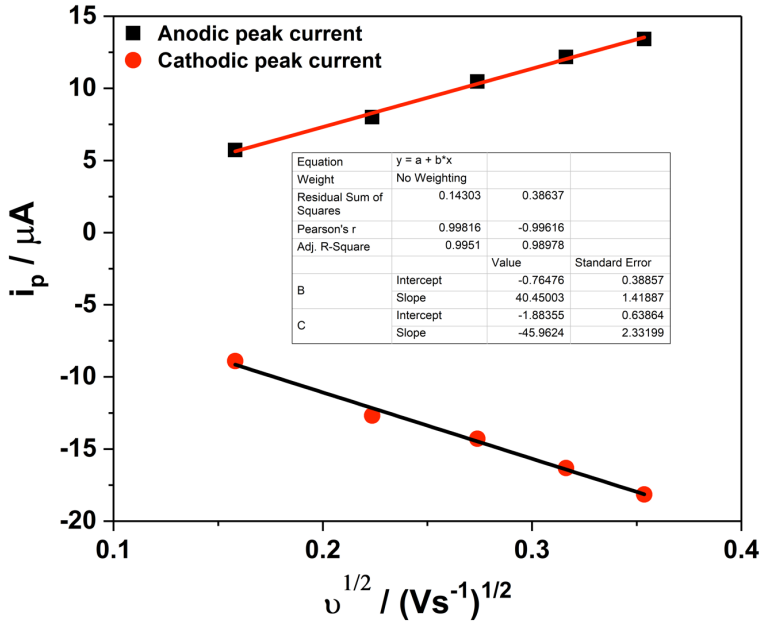


Figure S13. The plot of i_p *vs.* $\nu^{1/2}$ for [**Cu 1**] with the linear fitted slope for both anodic and cathodic peaks.

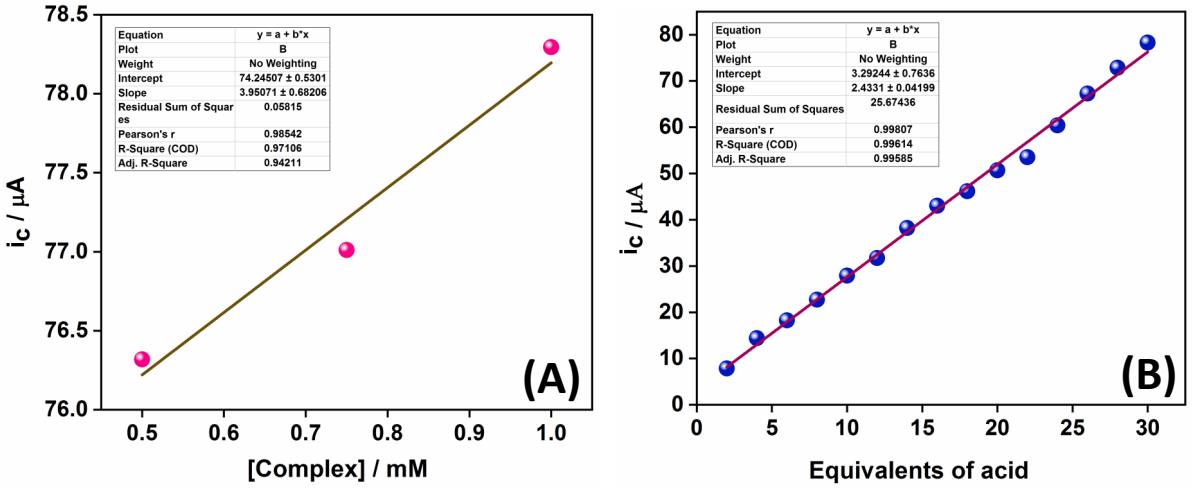
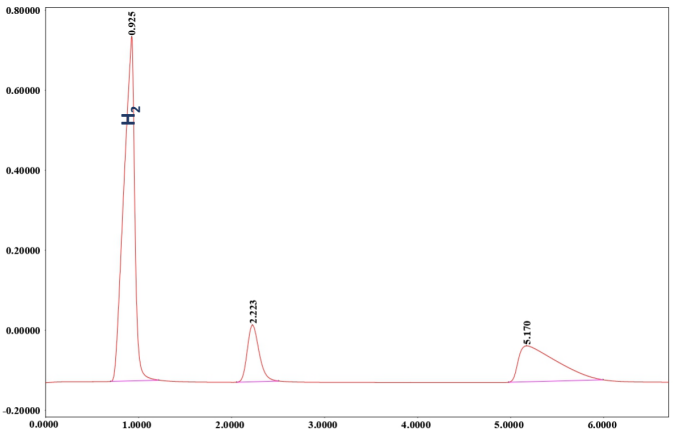
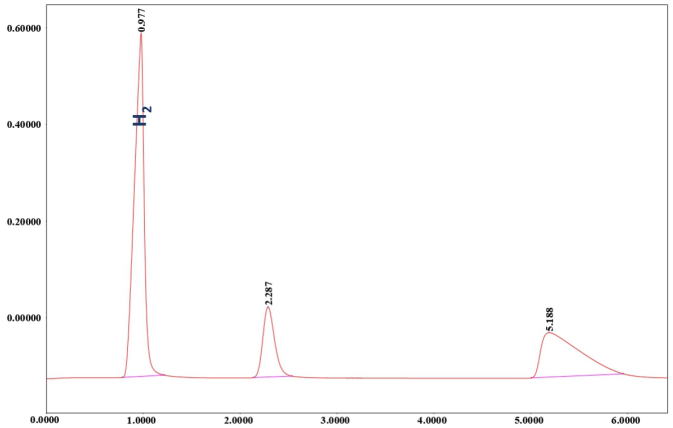


Figure S14. Dependence of the catalytic current (i_c) as a function of (a) the catalyst concentration and (b) AcOH concentration for [**Cu 1**]. Electrocatalytic condition: 1.0 mM of [**Cu 1**] in 95/5 (v/v) DMF/H_2O with 0.1 M TBAP as the supporting electrolyte under an inert atmosphere using the three-electrode configuration.



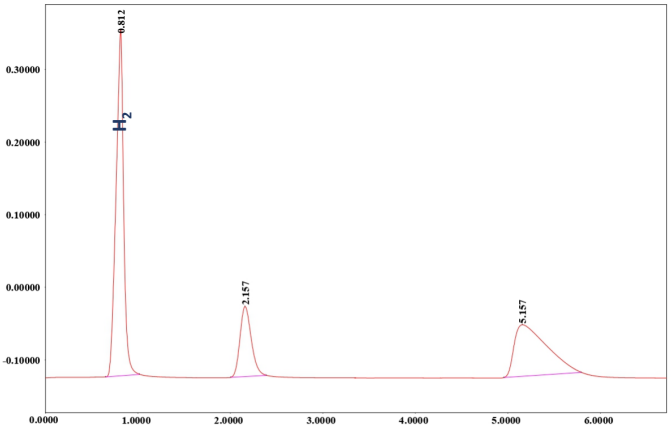
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.925	6965.816	BB	31.100	64.758
2	2.223	1252.335	BB	27.200	11.642
3	5.170	2538.598	BB	61.100	23.600

Figure S15. Gas chromatogram of H_2 gas from [**Cu 1**] evolved during the bulk electrolysis process. Electrolysis condition: 0.5 mM of [**Cu 1**] with the addition of 30 equivalent CH_3COOH in 95/5 (v/v) DMF/H_2O using 0.1 M TBAP as supporting electrolyte at a potential of -1.9 V *vs*. SCE under an inert atmosphere for a span of half an hour.



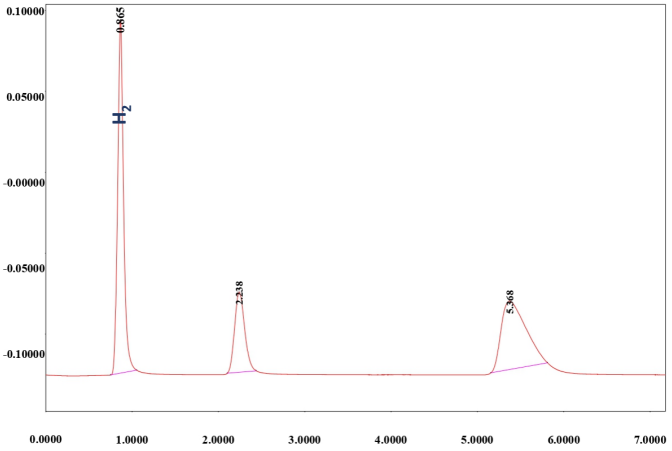
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.977	4958.842	BB	26.200	56.910
2	2.287	1217.733	BB	24.100	13.975
3	5.188	2536.977	BB	57.100	29.115

Figure S16. The gas chromatogram of H_2 gas from [**Cu 1**] evolved during the bulk electrolysis process. Electrolysis condition: 0.5 mM of [**Cu 1**] with the addition of 30 equivalent CH_3COOH in 95/5 (v/v) DMF/H_2O using 0.1 M TBAP as supporting electrolyte at a potential of -1.8 V *vs*. SCE under an inert atmosphere for a span of half an hour.



#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.812	2700.638	BB	22.100	51.529
2	2.157	814.909	BB	23.100	15.549
3	5.157	1725.429	BB	50.200	32.922

Figure S17. The gas chromatogram of H_2 gas from [**Cu 1**] evolved during the bulk electrolysis process. Electrolysis condition: 0.5 mM of [**Cu 1**] with the addition of 30 equivalent CH_3COOH in 95/5 (v/v) DMF/H_2O using 0.1 M TBAP as supporting electrolyte at a potential of -1.7 V *vs*. SCE under an inert atmosphere for a span of half an hour.



#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.865	1028.186	BB	18.100	45.409
2	2.238	400.259	BB	20.100	17.677
3	5.368	835.839	BB	39.300	36.914

Figure S18. The gas chromatogram of H_2 gas from [**Cu 1**] evolved during the bulk electrolysis process. Electrolysis condition: 0.5 mM of [**Cu 1**] with the addition of 30 equivalent CH_3COOH in 95/5 (v/v) DMF/H_2O using 0.1 M TBAP as supporting electrolyte at a potential of -1.6 V *vs*. SCE under an inert atmosphere for a span of half an hour.

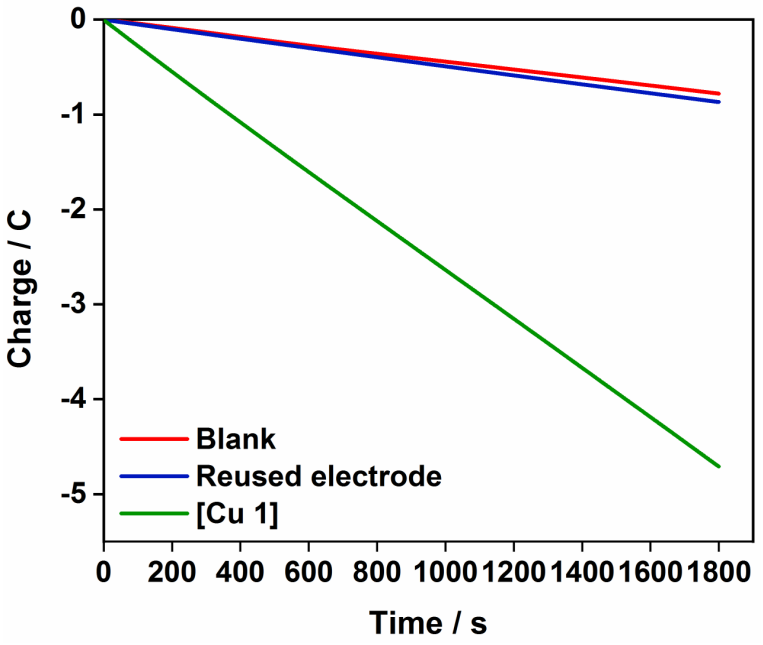


Figure S19. The charge build-up during the controlled potential electrolysis of [**Cu 1**] and reused electrode after electrolysis at -1.9 V *vs*. SCE. Electrolysis condition: 0.5 mM of the complex with 30 equivalent CH_3COOH in 95/5 (v/v) DMF/H_2O using 0.1 M TBAP as supporting electrolyte for a span of half an hour.

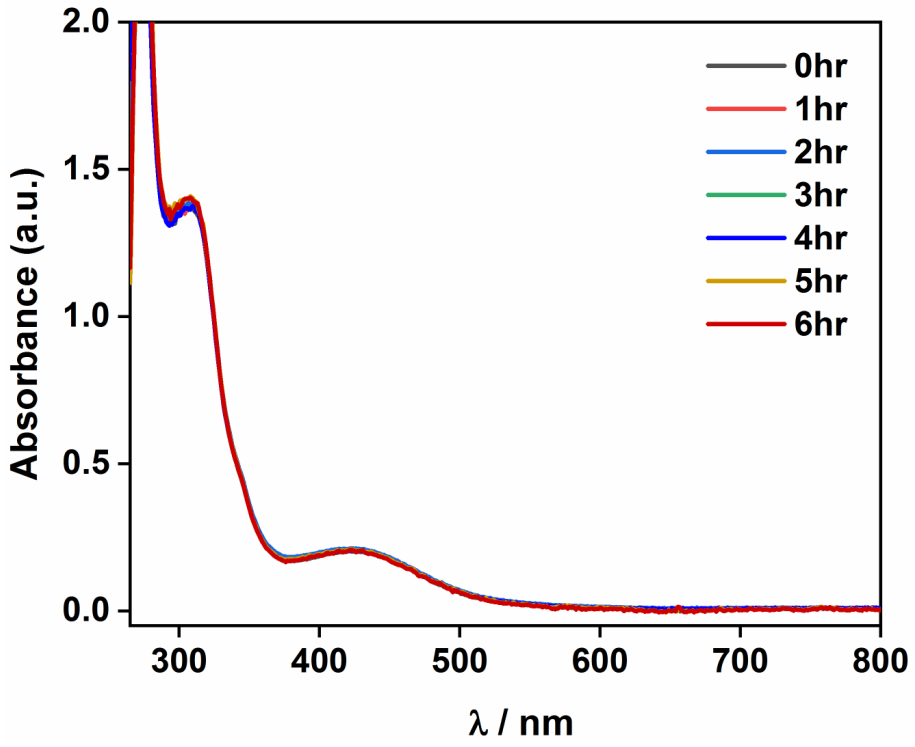


Figure S20. Time-dependent UV-Vis spectra of [**Cu 1**] (0.05 mM) in 95/5 (v/v) DMF/H_2O.

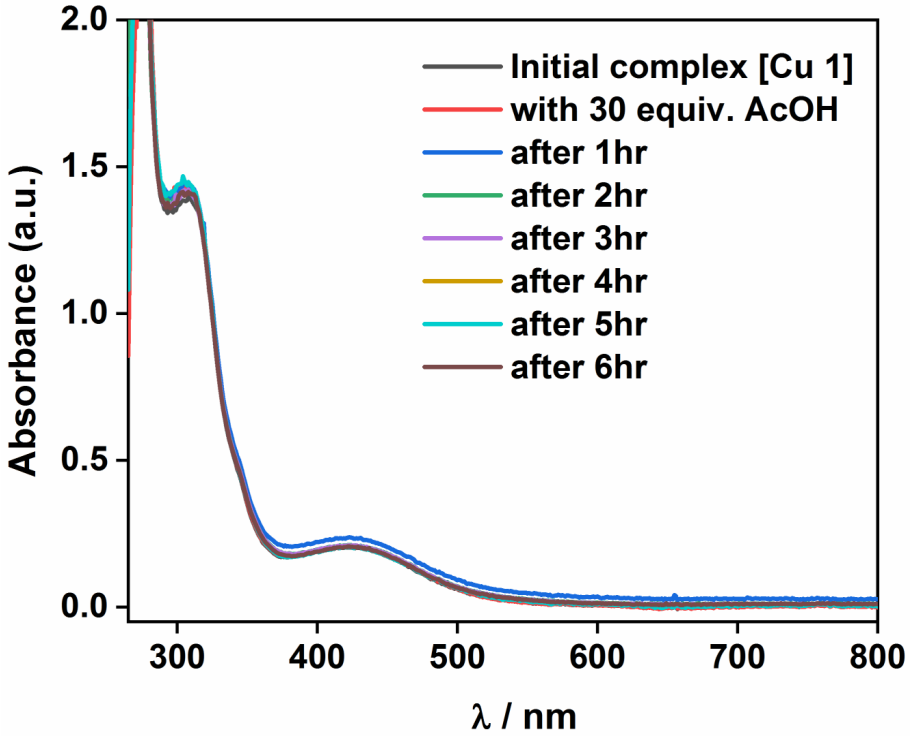


Figure S21. Time-dependent UV-Vis spectra of [**Cu 1**] (0.05 mM) in 95/5 (v/v) DMF/H_2O with the addition of 30 equivalent of CH_3COOH.

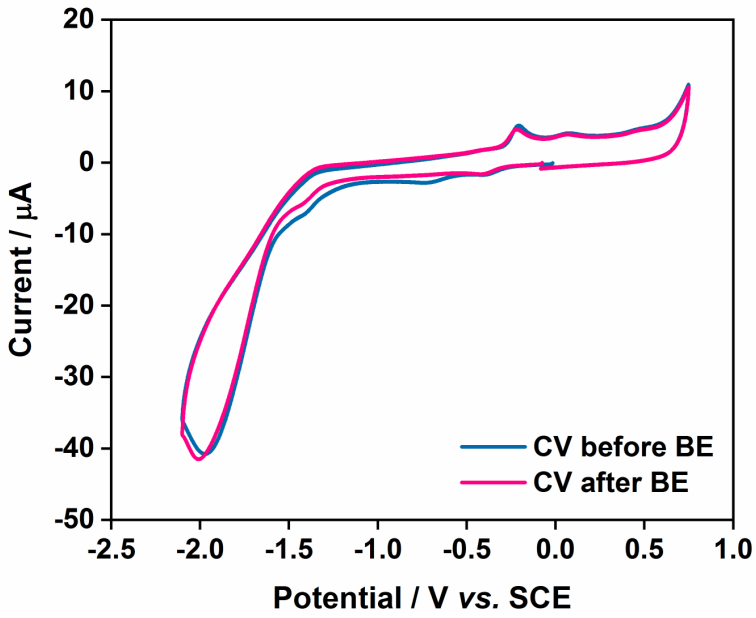


Figure S22. Cyclic voltammogram of complex [**Cu 1**] before and after the bulk electrolysis for half an hour at -1.6 V *vs*. SCE. Electrolysis condition: 0.05 mM of complex with the addition of 30 equivalent CH_3COOH in 95/5 (v/v) DMF/H_2O using 0.1 M TBAP as supporting electrolyte.

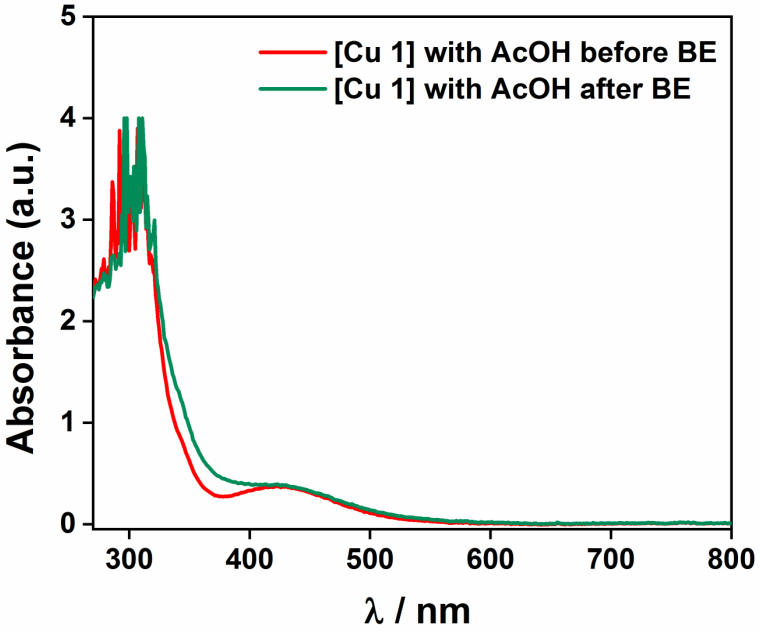


Figure S23. UV-Vis spectra of complex [**Cu 1**] before and after the bulk electrolysis for half an hour at -1.6 V *vs.* SCE. Electrolysis condition: 0.05 mM of the complex with the addition of 30 equivalent CH_3COOH in 95/5 (v/v) DMF/H_2O using 0.1 M TBAP as supporting electrolyte.

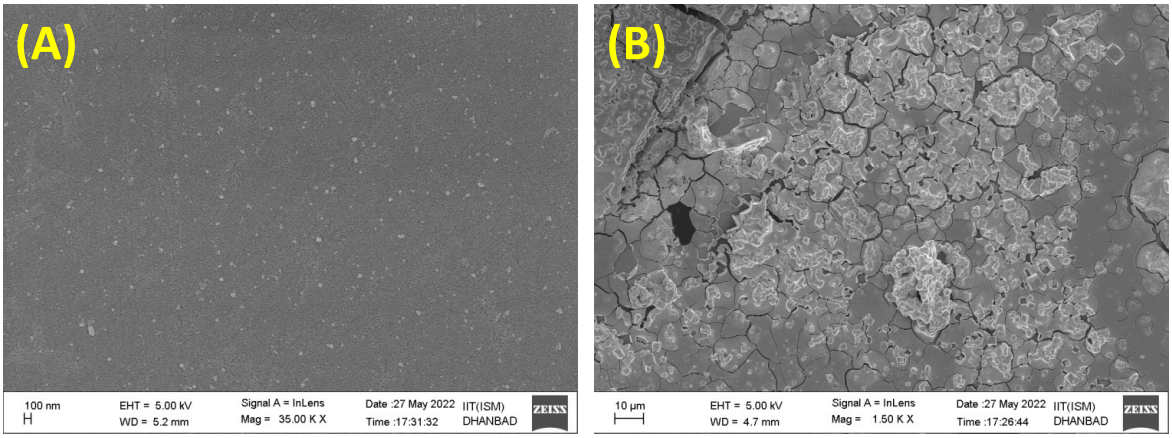


Figure S24. FESEM images of the glassy carbon plate (A) before and (B) after bulk electrolysis of [**Cu 1**] for half an hour at −1.6 V *vs.* SCE. Electrolysis condition: 0.05 mM of the complex with the addition of 30 equivalents CH_3COOH in 95/5 (v/v) DMF/H_2O using 0.1 M TBAP as the supporting electrolyte.

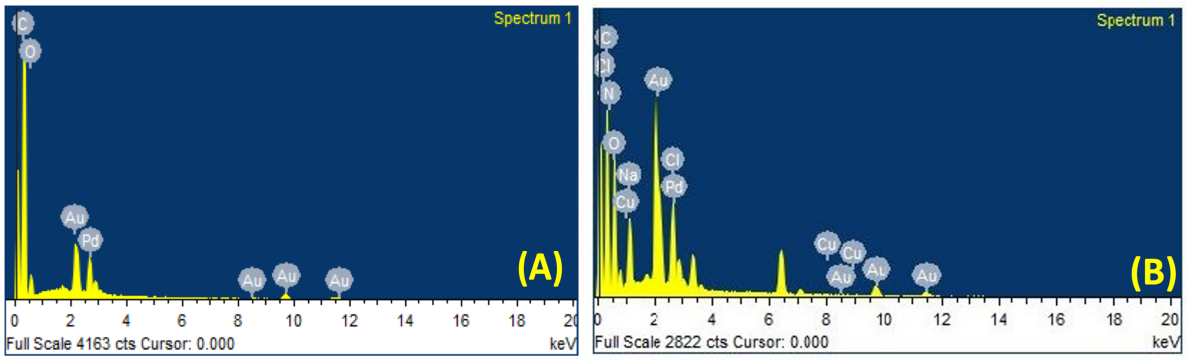


Figure S25. EDX data of glassy carbon plate (A) before bulk electrolysis and (B) after bulk electrolysis of [**Cu 1**] for half an hour at -1.6 V *vs*. SCE. Electrolysis condition: 0.05 mM of the complex with the addition of 30 equivalent CH_3COOH in 95/5 (v/v) DMF/H_2O using 0.1 M TBAP as supporting electrolyte. The surface of the electrode was coated with gold and palladium to make it current conductive.

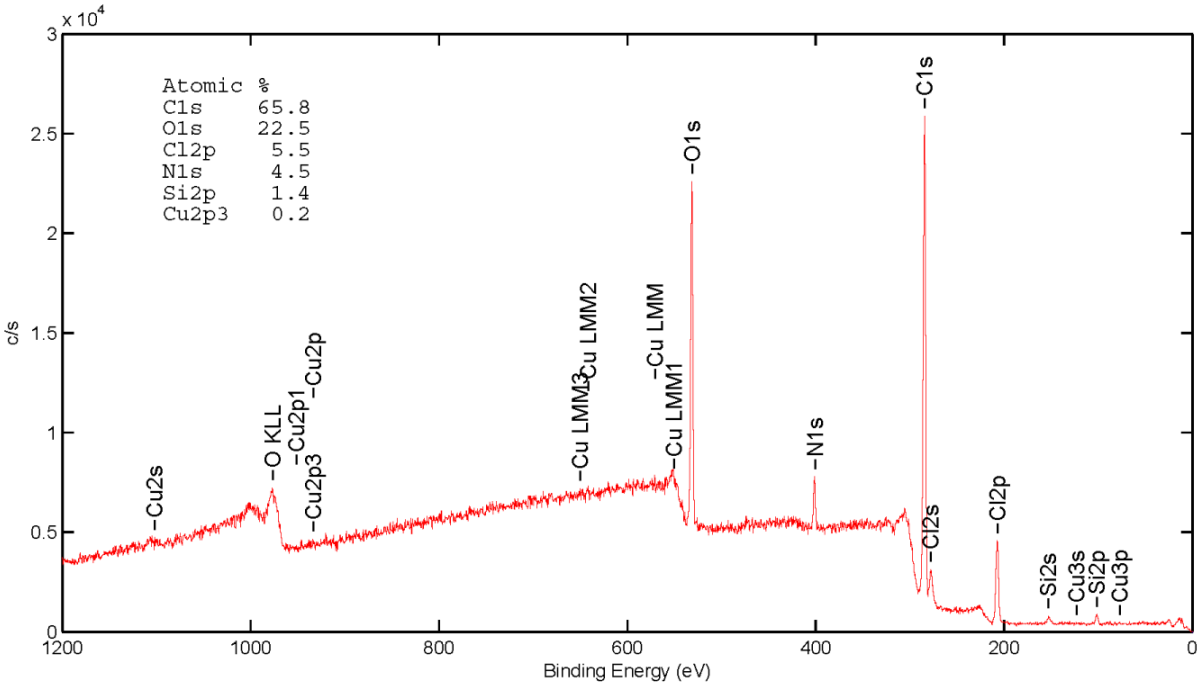


Figure S26. The XPS survey scan of complex **[Cu 1]** after controlled potential electrolysis at -1.6 V *vs*. SCE with the addition of 30 equivalent CH_3COOH in 95/5 (v/v) DMF/H_2O using 0.1 M TBAP as supporting electrolyte for a duration of half an hour.

Calculation

(A) Diamagnetic susceptibility (χ_D)

The diamagnetic susceptibility(X_D) are determined by the following expressions:
[**Cu 1**] represents $Cu_2C_{52}H_{32}N_8O_4$ for which χ_D [**Cu 1**] = -6089.59 × 10^{-12} m^3 mol^{-1}

(B) Evan's method

The magnetic susceptibility(χ_m) are determined by the following expressions:

$$\chi_m = \frac{6}{1000} \times \frac{1}{c} \times \frac{\Delta f}{f}$$

where, c = concentration of complex (mol/L), Δf = shift in the frequency of reference compound (Hz), f = frequency of spectrometer (Hz)
For **[Cu 1]**:
$c = 1.7\times10^{-3}$ mol/L
Δf = 0.02 ppm = 48 Hz
$f = 400\times10^{6}$ Hz
Now, $X_{m(\text{Cu 1})} = 0.07\times10^{-6}$ m^3 mol^{-1}

(C) Determination of effective magnetic moment (μ_{eff})

$$\chi_p = \chi_m - \chi_D$$

For **Cu 1**:
χ_p(**Cu 1**)= χ_m(**Cu 1**)- χ_D(**Cu 1**) = $(0.07\times10^{-6} - (-6089.59\times10^{-12}))$ m^3 mol^{-1}
Or, χ_p(**Cu 1**)= 0.07×10^{-6} m^3 mol^{-1}
Now, $\mu_{eff} = 798\sqrt{(\chi_m T)}$
Or, $\mu_{eff(\text{Cu 1})} = 3.63\ \mu_B$
For, one metal centre $\mu_{eff(\text{Cu 1})} = 1.81\ \mu_B$
Thus, n = 1.

Determination of no. of electron from bulk-electrolysis

Charge consumed at 2000 s is 0.51 C

No. of moles of [**Cu 1**] = 2.5 x 10^{-6}

Now, no. of electron **Cu 1** = $\frac{0.51}{96500} \times \frac{1}{2.5 \times 10^{-6}}$

Or, no. of electron consumed **Cu 1** = 2.11

Table S1. Crystal data and structure refinement for **Cu 1**.

Empirical formula	$C_{52}H_{36}N_8O_5Cu$
CCDC No.	2264293
Formula weight	977.99
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.5122(6)
b/Å	12.5503(7)
c/Å	15.0198(7)
α/°	100.619(4)
β/°	98.708(4)
γ/°	103.620(4)
Volume/Å³	2029.38(19)
Z	2
ρ_{calc}g/cm³	1.6004
μ/mm⁻¹	1.113
F(000)	1001.7
Crystal size/mm³	25 × 22 × 18
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.72 to 58.84
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 17, -20 ≤ l ≤ 19
Reflections collected	33134
Independent reflections	9807 [R_{int} = 0.0449, R_{sigma} = 0.0640]
Data/restraints/parameters	9807/0/607
Goodness-of-fit on F²	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0434, wR_2 = 0.0939
Final R indexes [all data]	R_1 = 0.0856, wR_2 = 0.1084
Largest diff. peak/hole / e Å⁻³	0.57/-0.73

Table S2. Selected bond lengths of **Cu 1**.

Atom	Atom	Length/Å
Cu1	O1	1.9076(18)
Cu1	O2	1.9663(18)
Cu1	N2	2.044(2)
Cu1	N8	2.140(2)
Cu1	N1	2.215(2)
Cu2	O4	1.9817(18)
Cu2	O3	1.9121(19)
Cu2	N6	2.031(2)
Cu2	N4	2.084(2)
Cu2	N5	2.207(2)

Table S3. Selected bond angles of **Cu 1**.

Atom	Atom	Atom	Angle/°
O2	Cu1	O1	85.69(8)
N2	Cu1	O1	166.80(9)
N2	Cu1	O2	81.85(8)
N8	Cu1	O1	94.53(9)
N8	Cu1	O2	126.90(8)
N8	Cu1	N2	96.41(8)
N1	Cu1	O1	81.17(8)
N1	Cu1	O2	127.37(8)
N1	Cu1	N2	103.03(8)
N1	Cu1	N8	104.89(8)
O3	Cu2	O4	89.92(8)
N6	Cu2	O4	82.30(8)
N6	Cu2	O3	171.89(8)
N4	Cu2	O4	132.93(9)
N4	Cu2	O3	91.13(8)
N4	Cu2	N6	95.84(8)
N5	Cu2	O4	115.20(8)
N5	Cu2	O3	81.04(9)
N5	Cu2	N6	100.18(9)
N5	Cu2	N4	111.41(8)

Table S4. Atomic and Weight % of elements on the electrode after electrolysis in EDX.

Elements	Blank		Cu 1	
	Weight %	Atomic %	Weight %	Atomic %
C	62.74	81.75	40.33	51.86
N	--	--	5.17	5.70
O	16.63	16.27	37.91	36.60
Na	--	--	4.39	2.95
Cu	--	--	4.83	2.11
Pd	4.97	0.73	0.03	0.01
Au	15.65	1.24	2.93	0.43
Total	100.00	--	100.00	--

Computational Details

Density functional theory (DFT) calculations were carried out using the Gaussian 09 program. Geometry optimization and frequency calculations of all molecules were performed using B3LYP functional. LANL2DZ basis set was used for Cu metal centers, and 6-31G* basis set was used for all other atoms (H, C, N, O). Unrestricted B3LYP (U-B3LYP) and restricted B3LYP (R-B3LYP) were employed for open-shell and close-shell electronic configurations, respectively. Single-point electronic energy of all optimized structures was carried out at the M06L[1] functional LANL2DZ basis set for Cu metal centres and 6-311++G(d, p) basis set for all other atoms. Frequency calculations distinguished the stationary points as transition states and intermediates. The transition states were identified by one imaginary frequency, confirmed by the IRC calculations, and no imaginary frequency existed for other intermediates. The solvent effect of dimethylformamide[2] (DMF, ε = 36.71, rsolv = 2.647, density = 0.00778, epsinf = 1.75) in the reaction was considered by the self-consistent reaction field approach using the conductor-like polarisable continuum model[3] (CPCM). We have calculated the low-spin to high-spin electronic structures of each molecule to decide the most stable electronic structure.

The total Gibbs free energy of each molecule was calculated using the equation

$$G = E_{sp} + G_{corr} + \Delta G_{sol} + \Delta G^{0/*} \quad (1)$$

E_{sp} was the single point electronic energy, and the G_{corr} was the thermal correction to Gibb's free energy. The free energy change (G_{sol}) was the difference between the free energies of the

gas and the solvent phase. The phase transfer free energy change ($\Delta G^{o/*}$) 1.9 kcal mol^{-1} was added to the electronic energy, which was associated with the phase change from the gas phase to 1 atm pressure to a standard state 1 M of concentration. The Gibbs free energy of a proton was taken as -263.6 kcal mol^{-1} for the protonation reaction according to the solvation energy considering the CPCM model of -257.3 kcal mol^{-1} energy[4,5], and the gas phase Gibbs free energy correction[6] of -6.3 kcal mol^{-1}.

The p*Ka* value for an acid-base equilibrium was determined by using the following equations-

$$HA = A^- + H^+ \quad (2)$$

$$K_a = -\frac{\Delta G^0_{solv}}{RTln(10)} \quad (3)$$

Where,

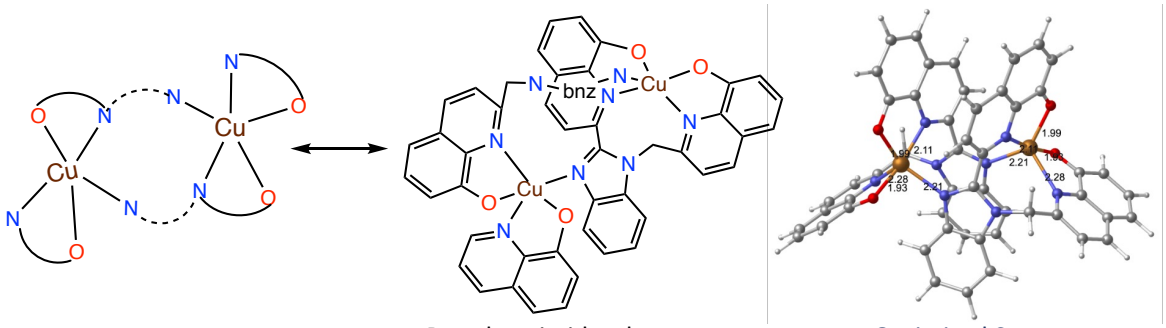
$$G_{sol} = [G(A_{gas}^-) - G(AH_{(gas)}) - \Delta G_{sol}(A^-) - \Delta G_{sol}(HA) - G(H^+)] \quad (4)$$

The term $G(AH_{(gas)})$ is the gas-phase free energy of protonated form, and $G(A_{gas}^-)$ is the gas-phase free energy of the deprotonated form of HA acid. $G_{sol}(A^-)$ and $G_{sol}(HA)$ are solvent phase-free energies of the deprotonated and protonated forms.

The redox potential values[7] for the electron transfer process were calculated using the thermodynamic cycle.

$$E^0 \text{ vs SHE} = -\frac{\Delta G^{0,red}_{sol}}{nF} - 4.281\ V \quad (5)$$

Here, $\Delta G^{0,red}_{sol}$ is the free energy difference between the reduced species and the oxidized species, F is Faraday's constant and n is the number of electrons transferred during the reduction process. The obtained E^o value concerned the SHE potential (i.e., -4.281 V) to get the final reduction potential.



Bnz= benzimidazole

Optimized Structure

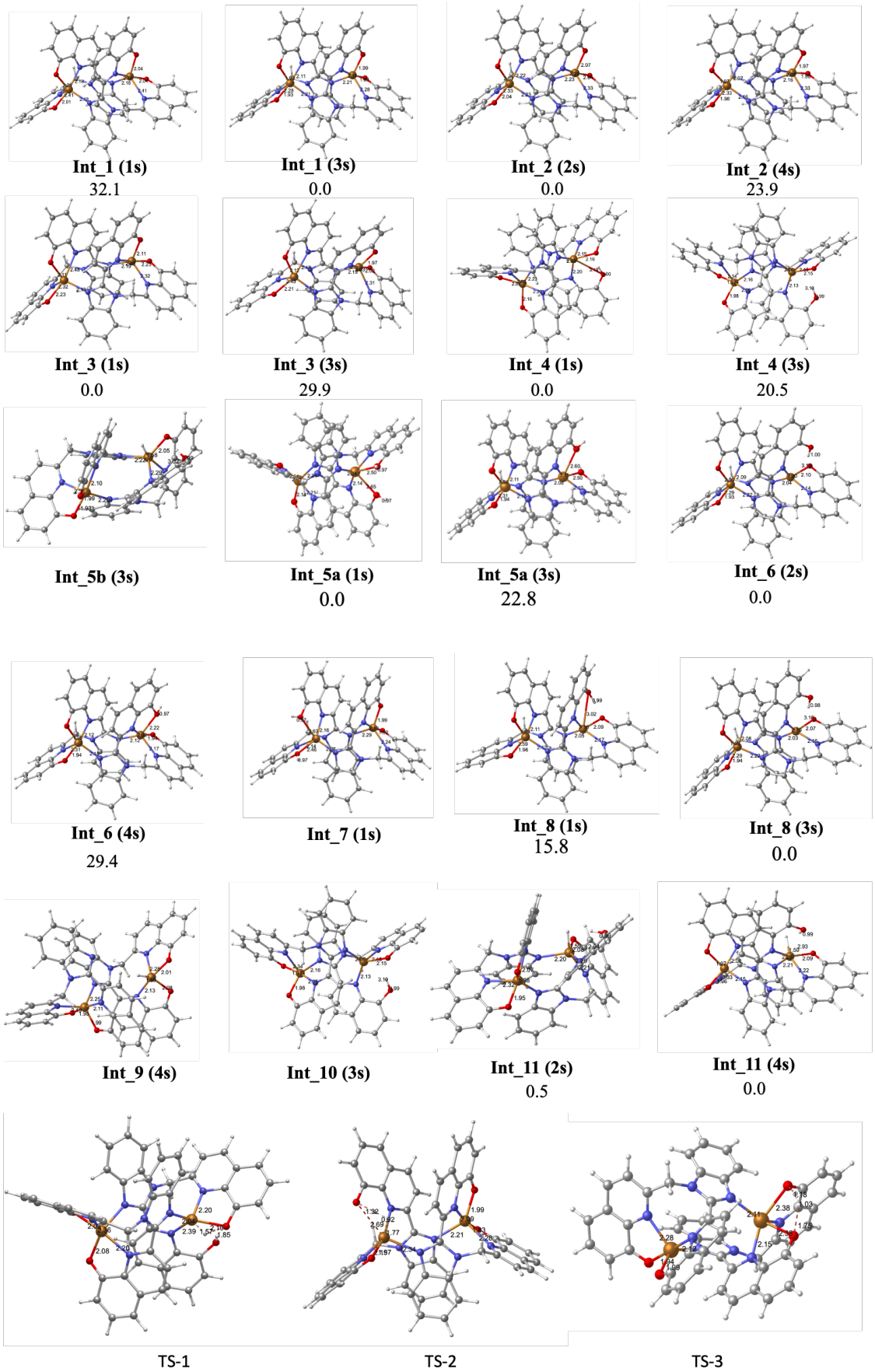


Figure S27. Structures of all intermediate with relative energy values considering the possible spin state.

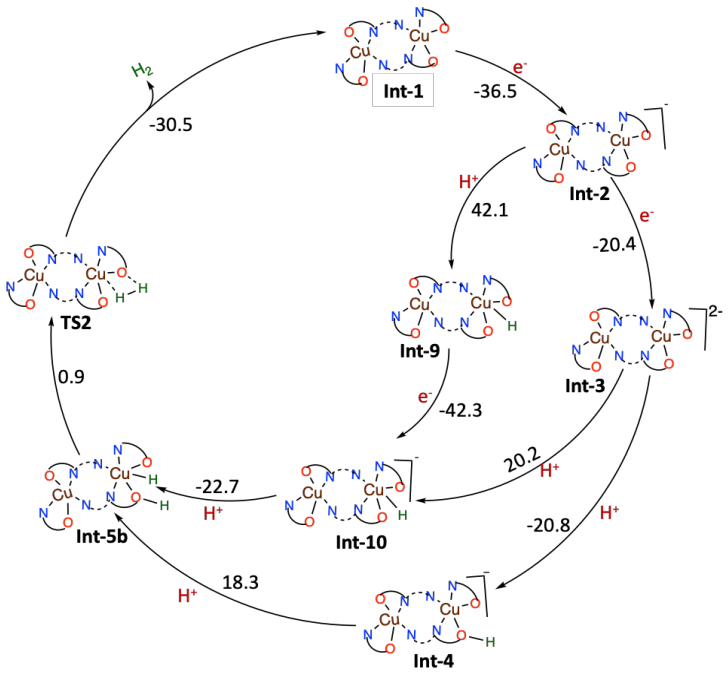


Figure S28. Possible reaction mechanism pathways for Cu bimetal-catalyzed hydrogen formation reaction (all energy values are shown in kcal mol^{-1}).

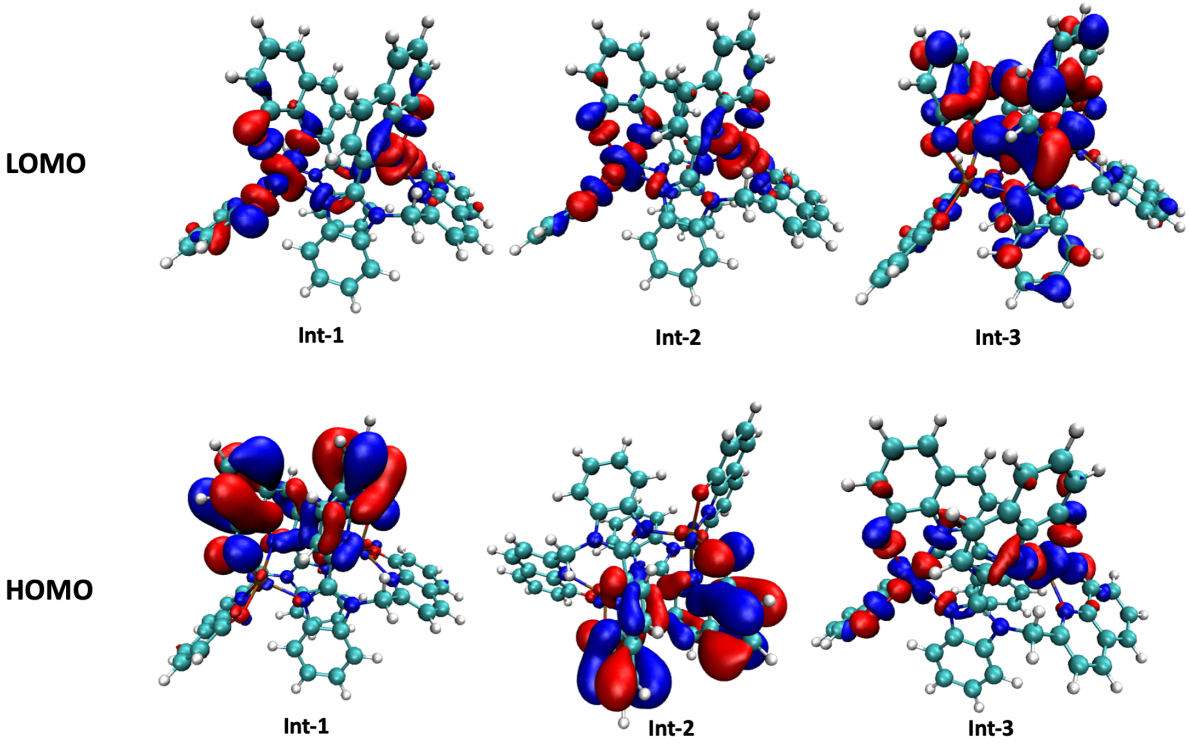


Figure S29. HOMO and LUMO in **int-1**, **int-2** and **int-3**.

Table S5. Experimental and theoretical bond length comparison.

Bond	Experimental Bond length	Bond length (B3LYP)
Cu1-O1	1.91 Å	1.93 Å
Cu1-N1	2.21 Å	2.28 Å
Cu1-N2	1.98 Å	2.11 Å
Cu1-N3	2.03 Å	2.21 Å
Cu1-O2	2.08 Å	1.99 Å

Table S6. p*K*a values of hydrogenation steps.

Sl. No.	**Protonated Form**	**Deprotonated Form**	**p*Ka values***
1	Int-8	Int-1	4.4
2	Int-6	Int-2	21.4
3	Int-5b	Int-4	-16.4
4	Int-7	Int-6	-8.8
5	Int-4	Int-3	22.3
6	Int-9	Int-2	-20.7
7	Int-5b	Int-10	9.3
8	Int-10	Int-3	-9.7
9	Int-4	Int-5a	10.4
10	Int-12	Int-6	-32.7

Table s7. Calculated redox potentials of all intermediates*

Sl. No.	Oxidized Form	Reduces Form	E^o values vs SHE (in V)	Experimental E^o values vs SHE (in V)
1	Int-1	Int-2	-0.58	-0.45 V
2	Int-2	Int-3	-0.67	-0.45 V
3	Int-8	Int-6	-0.37	NA
4	Int-6	Int-4	-1.42	-1.18 V (Considering pH AcOH in DMF 13.5)
5	Int-7	Int-5a	-1.32	NA
6	Int-9	Int-10	-0.82	NA
7	Int-5b	Int-12	-0.25	NA
*SHE = SCE-0.241+0.172 (liquid junction potential)				

Table S8. Mulliken Spin densities of selected atoms in different intermediates

Centers	Int-1	Int-2	Int-3	Int-5	TS-1
Cu (1)	0.5831	0.3370	NA	0.3246	0.0938
O (4)	0.1625	0.0598	NA	0.0557	0.0802
O (6)	0.1271	0.0432	NA	0.0006	0.0806
Cu (2)	0.5851	0.3366	NA	0.3776	0.5874
O (3)	0.1258	0.0431	NA	0.1364	0.1141
O (5)	0.1677	0.0596	NA	0.1485	0.1628

References

1. Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* **2008**, *120* (1), 215–241. https://doi.org/10.1007/s00214-007-0310-x.

2. Böes, E. S.; Livotto, P. R.; Stassen, H. Solvation of Monovalent Anions in Acetonitrile and N,N-Dimethylformamide: Parameterization of the IEF-PCM Model. *Chem. Phys.* **2006**, *331* (1), 142–158. https://doi.org/10.1016/j.chemphys.2006.08.028.

3. Tomasi, J.; Mennucci, B.; Cammi, R. Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* **2005**, *105* (8), 2999–3094. https://doi.org/10.1021/cr9904009.

4. *How to Predict the pKa of Any Compound in Any Solvent | ACS Omega*. https://pubs.acs.org/doi/10.1021/acsomega.2c01393?ref=pdf (accessed 2023-05-20).

5. Marković, Z.; Tošović, J.; Milenković, D.; Marković, S. Revisiting the Solvation Enthalpies and Free Energies of the Proton and Electron in Various Solvents. *Comput. Theor. Chem.* **2016**, *1077*, 11–17. https://doi.org/10.1016/j.comptc.2015.09.007.

6. Tissandier, M. D.; Cowen, K. A.; Feng, W. Y.; Gundlach, E.; Cohen, M. H.; Earhart, A. D.; Coe, J. V.; Tuttle, T. R. The Proton's Absolute Aqueous Enthalpy and Gibbs Free Energy of Solvation from Cluster-Ion Solvation Data. *J. Phys. Chem. A* **1998**, *102* (40), 7787–7794. https://doi.org/10.1021/jp982638r.

7. Baik, M.-H.; Friesner, R. A. Computing Redox Potentials in Solution: Density Functional Theory as A Tool for Rational Design of Redox Agents. *J. Phys. Chem. A* **2002**, *106* (32), 7407–7412. https://doi.org/10.1021/jp025853n.

Coordinates-

Int_1 (1s)

Cu	2.591000	0.424000	-0.786000
Cu	-2.591000	0.423000	0.786000
O	-3.352000	2.253000	1.270000
O	3.836000	-0.633000	-1.951000
O	-3.837000	-0.635000	1.950000
O	3.351000	2.254000	-1.270000
N	1.634000	1.676000	0.726000
N	0.815000	-0.596000	-1.539000
N	-1.634000	1.675000	-0.725000
N	-1.277000	-0.964000	-2.263000
N	-0.815000	-0.596000	1.541000
N	1.278000	-0.963000	2.263000
N	3.829000	-0.961000	0.755000
N	-3.829000	-0.962000	-0.756000
C	-0.360000	-0.051000	-1.797000
C	1.993000	2.969000	0.541000
C	0.695000	1.379000	1.624000
C	-0.695000	1.379000	-1.624000
C	0.360000	-0.050000	1.798000
C	2.990000	3.211000	-0.491000
C	-3.778000	-1.198000	-2.058000
C	1.436000	4.038000	1.310000
C	-1.994000	2.968000	-0.540000
C	3.779000	-1.197000	2.057000
C	-0.630000	-2.191000	-2.305000
C	0.684000	-1.946000	-1.851000
C	0.057000	2.370000	2.405000
H	-0.717000	2.080000	3.108000
C	-0.683000	-1.946000	1.853000
C	4.915000	-1.361000	0.047000
C	0.631000	-2.191000	2.307000

C	0.432000	3.689000	2.248000
H	-0.039000	4.467000	2.842000
C	-0.058000	2.370000	-2.405000
H	0.716000	2.080000	-3.107000
C	-1.063000	-3.459000	-2.703000
H	-2.079000	-3.638000	-3.040000
C	-4.900000	-1.090000	1.386000
C	-1.437000	4.038000	-1.310000
C	4.900000	-1.089000	-1.388000
C	-2.991000	3.210000	0.491000
C	-4.915000	-1.362000	-0.048000
C	2.585000	-0.675000	2.841000
H	2.666000	0.412000	2.936000
H	2.605000	-1.091000	3.855000
C	-2.584000	-0.676000	-2.842000
H	-2.665000	0.410000	-2.937000
H	-2.603000	-1.093000	-3.855000
C	-1.610000	-2.993000	1.783000
H	-2.623000	-2.805000	1.453000
C	-6.042000	-1.995000	-0.658000
C	1.611000	-2.994000	-1.780000
H	2.623000	-2.805000	-1.449000
C	-0.433000	3.688000	-2.248000
H	0.038000	4.467000	-2.842000
C	6.042000	-1.995000	0.656000
C	3.470000	4.537000	-0.599000
H	4.243000	4.739000	-1.334000
C	-5.956000	-2.232000	-2.052000
H	-6.783000	-2.718000	-2.564000
C	1.914000	5.354000	1.104000
H	1.509000	6.172000	1.693000
C	-4.831000	-1.846000	-2.748000
H	-4.750000	-2.022000	-3.817000
C	-0.130000	-4.488000	-2.628000
H	-0.422000	-5.492000	-2.923000
C	1.185000	-4.257000	-2.174000
H	1.883000	-5.089000	-2.133000
C	2.919000	5.572000	0.169000
H	3.295000	6.583000	0.024000
C	1.065000	-3.458000	2.705000
H	2.081000	-3.637000	3.041000
C	-1.184000	-4.257000	2.177000
H	-1.881000	-5.089000	2.138000
C	4.832000	-1.845000	2.746000
H	4.751000	-2.022000	3.815000
C	-1.916000	5.353000	-1.104000
H	-1.511000	6.171000	-1.693000
C	-3.471000	4.535000	0.599000
H	-4.245000	4.737000	1.334000
C	-7.168000	-2.336000	0.134000
H	-8.025000	-2.814000	-0.332000
C	7.168000	-2.336000	-0.136000
H	8.025000	-2.814000	0.329000
C	6.074000	-1.404000	-2.108000
H	6.087000	-1.182000	-3.170000
C	5.956000	-2.232000	2.050000
H	6.784000	-2.719000	2.561000
C	-2.921000	5.571000	-0.169000
H	-3.297000	6.581000	-0.024000
C	-7.166000	-2.032000	1.487000
H	-8.036000	-2.282000	2.089000
C	-6.075000	-1.405000	2.106000
H	-6.088000	-1.183000	3.168000
C	0.131000	-4.487000	2.631000
H	0.424000	-5.491000	2.926000
C	7.165000	-2.032000	-1.489000
H	8.035000	-2.282000	-2.092000

Int_1 (3s)

Cu	2.664000	0.519000	-0.628000
Cu	-2.664000	0.520000	0.628000
O	-3.554000	2.260000	0.985000
O	3.824000	-0.378000	-1.889000
O	-3.824000	-0.377000	1.889000
O	3.555000	2.259000	-0.985000
N	1.618000	1.709000	0.771000
N	0.913000	-0.551000	-1.438000
N	-1.618000	1.709000	-0.771000
N	-1.147000	-0.955000	-2.232000
N	-0.913000	-0.551000	1.438000
N	1.146000	-0.955000	2.232000
N	3.732000	-0.936000	0.766000
N	-3.732000	-0.935000	-0.766000
C	-0.263000	-0.026000	-1.740000
C	2.022000	3.004000	0.660000
C	0.624000	1.399000	1.606000
C	-0.624000	1.399000	-1.606000
C	0.263000	-0.026000	1.739000
C	3.087000	3.248000	-0.286000
C	-3.634000	-1.243000	-2.050000
C	1.424000	4.062000	1.419000
C	-2.021000	3.005000	-0.660000
C	3.633000	-1.243000	2.050000
C	-0.479000	-2.173000	-2.246000
C	0.814000	-1.906000	-1.749000
C	-0.047000	2.382000	2.371000
H	-0.865000	2.084000	3.017000
C	-0.815000	-1.905000	1.749000
C	4.794000	-1.390000	0.042000
C	0.479000	-2.173000	2.246000
C	0.355000	3.697000	2.276000
H	-0.149000	4.465000	2.857000
C	0.047000	2.382000	-2.371000
H	0.866000	2.083000	-3.017000
C	-0.882000	-3.447000	-2.653000
H	-1.885000	-3.641000	-3.022000
C	-4.816000	-1.039000	1.363000
C	-1.422000	4.062000	-1.420000
C	4.816000	-1.040000	-1.363000
C	-3.086000	3.249000	0.286000
C	-4.794000	-1.389000	-0.042000
C	2.452000	-0.694000	2.832000
H	2.550000	0.389000	2.937000
H	2.451000	-1.122000	3.841000
C	-2.453000	-0.694000	-2.832000
H	-2.551000	0.390000	-2.937000
H	-2.451000	-1.121000	-3.841000

C	-1.752000	-2.941000	1.645000
H	-2.751000	-2.750000	1.276000
C	-5.841000	-2.174000	-0.625000
C	1.751000	-2.942000	-1.645000
H	2.750000	-2.751000	-1.276000
C	-0.354000	3.697000	-2.276000
H	0.150000	4.465000	-2.857000
C	5.840000	-2.175000	0.626000
C	3.541000	4.573000	-0.388000
H	4.350000	4.787000	-1.079000
C	-5.710000	-2.470000	-2.004000
H	-6.478000	-3.062000	-2.497000
C	1.916000	5.376000	1.262000
H	1.474000	6.189000	1.831000
C	-4.617000	-2.018000	-2.711000
H	-4.504000	-2.244000	-3.767000
C	0.061000	-4.463000	-2.545000
H	-0.207000	-5.472000	-2.846000
C	1.357000	-4.212000	-2.048000
H	2.065000	-5.033000	-1.982000
C	2.958000	5.601000	0.374000
H	3.340000	6.612000	0.255000
C	0.881000	-3.447000	2.653000
H	1.883000	-3.641000	3.022000
C	-1.358000	-4.212000	2.048000
H	-2.066000	-5.032000	1.982000
C	4.616000	-2.018000	2.711000
H	4.503000	-2.245000	3.768000
C	-1.913000	5.377000	-1.262000
H	-1.471000	6.189000	-1.831000
C	-3.539000	4.575000	0.388000
H	-4.348000	4.789000	1.079000
C	-6.920000	-2.605000	0.182000
H	-7.718000	-3.195000	-0.257000
C	6.919000	-2.605000	-0.181000
H	7.718000	-3.196000	0.258000
C	5.916000	-1.487000	-2.110000
H	5.955000	-1.230000	-3.163000
C	5.709000	-2.471000	2.005000
H	6.477000	-3.063000	2.497000
C	-2.955000	5.602000	-0.374000
H	-3.337000	6.613000	-0.255000
C	-6.936000	-2.254000	1.521000
H	-7.766000	-2.578000	2.145000
C	-5.916000	-1.485000	2.110000
H	-5.955000	-1.228000	3.164000
C	-0.063000	-4.463000	2.545000
H	0.205000	-5.472000	2.847000
C	6.936000	-2.255000	-1.521000
H	7.766000	-2.579000	-2.145000

Int_2 (2s)

Cu	2.710000	0.488000	-0.688000
Cu	-2.710000	0.488000	0.688000
O	-3.585000	2.330000	1.023000
O	3.989000	-0.499000	-1.937000
O	-3.990000	-0.499000	1.937000
O	3.585000	2.329000	-1.023000
N	1.657000	1.762000	0.788000
N	0.898000	-0.485000	-1.555000
N	-1.657000	1.763000	-0.788000
N	-1.211000	-0.874000	-2.230000
N	-0.898000	-0.485000	1.555000
N	1.211000	-0.875000	2.230000
N	3.816000	-0.979000	0.742000
N	-3.816000	-0.979000	-0.742000
C	-0.293000	0.047000	-1.773000
C	2.051000	3.053000	0.646000
C	0.642000	1.471000	1.601000
C	-0.642000	1.471000	-1.601000
C	0.293000	0.047000	1.773000
C	3.125000	3.294000	-0.313000
C	-3.691000	-1.232000	-2.036000
C	1.439000	4.125000	1.378000
C	-2.050000	3.053000	-0.646000
C	3.691000	-1.232000	2.036000
C	-0.548000	-2.090000	-2.309000
C	0.775000	-1.831000	-1.887000
C	-0.065000	2.467000	2.317000
H	-0.914000	2.182000	2.929000
C	-0.775000	-1.831000	1.887000
C	4.862000	-1.499000	0.049000
C	0.548000	-2.090000	2.309000
C	0.342000	3.777000	2.209000
H	-0.184000	4.560000	2.751000
C	0.066000	2.467000	-2.317000
H	0.915000	2.182000	-2.929000
C	-0.972000	-3.357000	-2.719000
H	-1.995000	-3.546000	-3.026000
C	-4.916000	-1.194000	1.380000
C	-1.438000	4.125000	-1.378000
C	4.915000	-1.194000	-1.381000
C	-3.124000	3.295000	0.313000
C	-4.862000	-1.499000	-0.049000
C	2.533000	-0.594000	2.784000
H	2.654000	0.491000	2.789000
H	2.543000	-0.936000	3.826000
C	-2.533000	-0.594000	-2.784000
H	-2.654000	0.491000	-2.789000
H	-2.542000	-0.936000	-3.826000
C	-1.719000	-2.865000	1.867000
H	-2.738000	-2.668000	1.565000
C	-5.868000	-2.311000	-0.673000
C	1.718000	-2.865000	-1.866000
H	2.738000	-2.668000	-1.564000
C	-0.341000	3.777000	-2.209000
H	0.184000	4.560000	-2.751000
C	5.868000	-2.312000	0.673000
C	3.582000	4.630000	-0.398000
H	4.396000	4.841000	-1.085000
C	-5.707000	-2.553000	-2.061000
H	-6.443000	-3.163000	-2.582000
C	1.932000	5.439000	1.222000
H	1.472000	6.256000	1.772000
C	-4.630000	-2.026000	-2.738000
H	-4.495000	-2.208000	-3.801000
C	-0.020000	-4.373000	-2.692000

H	-0.307000	-5.377000	-2.996000
C	1.303000	-4.129000	-2.272000
H	2.017000	-4.948000	-2.268000
C	2.991000	5.657000	0.350000
H	3.373000	6.671000	0.230000
C	0.971000	-3.357000	2.719000
H	1.995000	-3.546000	3.026000
C	-1.303000	-4.129000	2.273000
H	-2.017000	-4.948000	2.269000
C	4.630000	-2.026000	2.737000
H	4.495000	-2.208000	3.801000
C	-1.931000	5.439000	-1.222000
H	-1.472000	6.256000	-1.772000
C	-3.581000	4.630000	0.398000
H	-4.395000	4.842000	1.086000
C	-6.938000	-2.821000	0.097000
H	-7.701000	-3.433000	-0.377000
C	6.938000	-2.821000	-0.097000
H	7.700000	-3.434000	0.376000
C	6.014000	-1.736000	-2.086000
H	6.081000	-1.524000	-3.149000
C	5.707000	-2.553000	2.060000
H	6.442000	-3.164000	2.581000
C	-2.990000	5.658000	-0.350000
H	-3.372000	6.671000	-0.230000
C	-6.987000	-2.521000	1.451000
H	-7.810000	-2.910000	2.049000
C	-6.015000	-1.736000	2.085000
H	-6.082000	-1.524000	3.149000
C	0.020000	-4.373000	2.692000
H	0.306000	-5.377000	2.997000
C	6.986000	-2.522000	-1.452000
H	7.810000	-2.911000	-2.050000

Int_2 (4s)

Cu	2.669000	0.554000	-0.659000
Cu	-2.669000	0.554000	0.659000
O	-3.718000	2.211000	0.840000
O	3.917000	-0.374000	-1.880000
O	-3.917000	-0.374000	1.880000
O	3.718000	2.211000	-0.840000
N	1.611000	1.694000	0.704000
N	0.994000	-0.545000	-1.453000
N	-1.611000	1.694000	-0.704000
N	-1.101000	-0.936000	-2.163000
N	-0.994000	-0.545000	1.453000
N	1.101000	-0.936000	2.163000
N	3.731000	-0.952000	0.770000
N	-3.731000	-0.952000	-0.770000
C	-0.200000	-0.003000	-1.685000
C	2.044000	2.999000	0.636000
C	0.551000	1.405000	1.500000
C	-0.551000	1.405000	-1.500000
C	0.200000	-0.003000	1.685000
C	3.194000	3.222000	-0.192000
C	-3.590000	-1.239000	-2.053000
C	1.396000	4.065000	1.324000
C	-2.044000	2.999000	-0.636000
C	3.590000	-1.239000	2.053000
C	-0.428000	-2.145000	-2.250000
C	0.890000	-1.886000	-1.810000
C	-0.162000	2.411000	2.184000
H	-1.021000	2.126000	2.784000
C	-0.890000	-1.886000	1.810000
C	4.804000	-1.416000	0.081000
C	0.428000	-2.145000	2.250000
C	0.239000	3.729000	2.093000
H	-0.304000	4.510000	2.617000
C	0.162000	2.411000	-2.184000
H	1.021000	2.126000	-2.784000
C	-0.841000	-3.406000	-2.684000
H	-1.860000	-3.592000	-3.009000
C	-4.865000	-1.063000	1.331000
C	-1.396000	4.065000	-1.324000
C	4.865000	-1.063000	-1.331000
C	-3.194000	3.222000	0.192000
C	-4.804000	-1.416000	-0.081000
C	2.393000	-0.652000	2.780000
H	2.493000	0.436000	2.824000
H	2.369000	-1.029000	3.809000
C	-2.393000	-0.652000	-2.780000
H	-2.493000	0.436000	-2.824000
H	-2.369000	-1.029000	-3.809000
C	-1.833000	-2.919000	1.791000
H	-2.848000	-2.734000	1.466000
C	-5.823000	-2.214000	-0.695000
C	1.833000	-2.919000	-1.791000
H	2.848000	-2.734000	-1.466000
C	-0.239000	3.729000	-2.093000
H	0.304000	4.510000	-2.617000
C	5.823000	-2.214000	0.695000
C	3.695000	4.535000	-0.259000
H	4.574000	4.719000	-0.871000
C	-5.648000	-2.498000	-2.073000
H	-6.393000	-3.100000	-2.590000
C	1.927000	5.368000	1.207000
H	1.442000	6.191000	1.726000
C	-4.545000	-2.021000	-2.748000
H	-4.400000	-2.237000	-3.804000
C	0.113000	-4.423000	-2.662000
H	-0.167000	-5.422000	-2.986000
C	1.426000	-4.181000	-2.219000
H	2.143000	-4.998000	-2.214000
C	3.061000	5.579000	0.431000
H	3.470000	6.585000	0.349000
C	0.841000	-3.406000	2.684000
H	1.860000	-3.592000	3.009000
C	-1.426000	-4.181000	2.219000
H	-2.143000	-4.998000	2.214000
C	4.545000	-2.021000	2.748000
H	4.400000	-2.237000	3.804000
C	-1.927000	5.368000	-1.207000
H	-1.441000	6.191000	-1.726000
C	-3.695000	4.535000	0.260000
H	-4.574000	4.719000	0.871000
C	-6.916000	-2.669000	0.080000
H	-7.693000	-3.271000	-0.382000

C	6.916000	-2.669000	-0.080000
H	7.693000	-3.271000	0.382000
C	5.978000	-1.549000	-2.045000
H	6.050000	-1.301000	-3.099000
C	5.648000	-2.498000	2.073000
H	6.393000	-3.100000	2.590000
C	-3.061000	5.579000	-0.431000
H	-3.470000	6.585000	-0.349000
C	-6.967000	-2.328000	1.423000
H	-7.806000	-2.674000	2.025000
C	-5.978000	-1.549000	2.045000
H	-6.050000	-1.301000	3.099000
C	-0.113000	-4.423000	2.662000
H	0.167000	-5.422000	2.986000
C	6.967000	-2.328000	-1.423000
H	7.806000	-2.674000	-2.025000

Int_3 (1s)

Cu	2.836000	0.419000	-0.766000
Cu	-2.836000	0.419000	0.766000
O	-3.705000	2.341000	0.834000
O	4.373000	-0.640000	-1.983000
O	-4.373000	-0.640000	1.983000
O	3.705000	2.341000	-0.834000
N	1.650000	1.831000	0.897000
N	1.032000	-0.336000	-1.746000
N	-1.650000	1.831000	-0.897000
N	-1.143000	-0.781000	-2.158000
N	-1.032000	-0.336000	1.746000
N	1.143000	-0.781000	2.158000
N	3.883000	-1.051000	0.688000
N	-3.883000	-1.051000	-0.688000
C	-0.194000	0.169000	-1.810000
C	2.069000	3.103000	0.736000
C	0.551000	1.582000	1.607000
C	-0.551000	1.582000	-1.607000
C	0.194000	0.169000	1.810000
C	3.223000	3.304000	-0.154000
C	-3.627000	-1.271000	-1.975000
C	1.417000	4.211000	1.379000
C	-2.069000	3.103000	-0.736000
C	3.627000	-1.271000	1.975000
C	-0.457000	-1.969000	-2.354000
C	0.901000	-1.675000	-2.098000
C	-0.223000	2.613000	2.198000
H	-1.148000	2.364000	2.709000
C	-0.901000	-1.675000	2.098000
C	4.956000	-1.647000	0.106000
C	0.457000	-1.969000	2.354000
C	0.226000	3.909000	2.097000
H	-0.339000	4.721000	2.550000
C	0.223000	2.613000	-2.198000
H	1.148000	2.364000	-2.709000
C	-0.882000	-3.241000	-2.752000
H	-1.929000	-3.462000	-2.926000
C	-5.182000	-1.365000	1.324000
C	-1.417000	4.211000	-1.379000
C	5.182000	-1.365000	-1.324000
C	-3.223000	3.304000	0.154000
C	-4.956000	-1.647000	-0.106000
C	2.498000	-0.511000	2.645000
H	2.670000	0.557000	2.517000
H	2.515000	-0.738000	3.719000
C	-2.498000	-0.511000	-2.645000
H	-2.670000	0.557000	-2.517000
H	-2.515000	-0.738000	-3.719000
C	-1.879000	-2.665000	2.249000
H	-2.920000	-2.412000	2.093000
C	-5.851000	-2.508000	-0.834000
C	1.878000	-2.665000	-2.249000
H	2.920000	-2.412000	-2.093000
C	-0.226000	3.909000	-2.097000
H	0.339000	4.721000	-2.550000
C	5.851000	-2.508000	0.834000
C	3.727000	4.634000	-0.200000
H	4.601000	4.815000	-0.821000
C	-5.542000	-2.725000	-2.200000
H	-6.184000	-3.374000	-2.794000
C	1.956000	5.509000	1.250000
H	1.463000	6.350000	1.733000
C	-4.445000	-2.116000	-2.765000
H	-4.200000	-2.268000	-3.814000
C	0.103000	-4.218000	-2.891000
H	-0.188000	-5.223000	-3.192000
C	1.460000	-3.932000	-2.647000
H	2.200000	-4.719000	-2.775000
C	3.101000	5.685000	0.477000
H	3.518000	6.689000	0.379000
C	0.882000	-3.241000	2.752000
H	1.929000	-3.462000	2.926000
C	-1.460000	-3.932000	2.647000
H	-2.200000	-4.719000	2.775000
C	4.444000	-2.116000	2.765000
H	4.200000	-2.268000	3.814000
C	-1.956000	5.509000	-1.250000
H	-1.463000	6.350000	-1.733000
C	-3.727000	4.634000	0.200000
H	-4.601000	4.815000	0.821000
C	-6.969000	-3.085000	-0.190000
H	-7.639000	-3.733000	-0.752000
C	6.969000	-3.085000	0.190000
H	7.639000	-3.733000	0.752000
C	6.335000	-1.978000	-1.893000
H	6.529000	-1.780000	-2.945000
C	5.542000	-2.725000	2.200000
H	6.184000	-3.374000	2.794000
C	-3.101000	5.685000	-0.477000
H	-3.518000	6.689000	-0.379000
C	-7.186000	-2.803000	1.154000
H	-8.050000	-3.244000	1.654000
C	-6.335000	-1.978000	1.893000
H	-6.529000	-1.780000	2.945000
C	-0.103000	-4.218000	2.891000
H	0.188000	-5.223000	3.192000
C	7.186000	-2.803000	-1.154000
H	8.050000	-3.244000	-1.654000

Int_4 (1s)

Cu	2.254000	-0.121000	-0.497000
Cu	-2.483000	0.697000	0.953000
O	-2.969000	2.748000	1.412000
O	3.888000	-0.147000	-1.904000
O	-4.027000	-0.363000	1.808000
O	4.577000	2.057000	-0.559000
N	2.082000	1.596000	0.863000
N	0.550000	-0.797000	-1.374000
N	-1.540000	1.798000	-0.706000
N	-1.459000	-0.943000	-2.351000
N	-0.738000	-0.275000	1.943000
N	1.371000	-0.940000	2.382000
N	3.756000	-1.214000	0.585000
N	-3.987000	-0.779000	-0.925000
C	-0.530000	-0.126000	-1.759000
C	2.550000	2.859000	0.605000
C	0.994000	1.451000	1.627000
C	-0.711000	1.340000	-1.647000
C	0.534000	0.086000	1.960000
C	3.775000	3.050000	-0.134000
C	-3.952000	-0.999000	-2.227000
C	1.857000	4.021000	1.088000
C	-1.746000	3.134000	-0.599000
C	3.752000	-1.579000	1.857000
C	-0.951000	-2.231000	-2.324000
C	0.318000	-2.125000	-1.716000
C	0.243000	2.544000	2.124000
H	-0.675000	2.361000	2.669000
C	-0.762000	-1.597000	2.368000
C	4.709000	-1.678000	-0.262000
C	0.553000	-2.029000	2.643000
C	0.669000	3.815000	1.834000
H	0.095000	4.676000	2.165000
C	-0.032000	2.197000	-2.547000
H	0.656000	1.773000	-3.273000
C	-1.461000	-3.450000	-2.777000
H	-2.449000	-3.525000	-3.219000
C	-5.052000	-0.874000	1.231000
C	-1.163000	4.079000	-1.515000
C	4.723000	-1.095000	-1.598000
C	-2.574000	3.579000	0.531000
C	-5.080000	-1.133000	-0.213000
C	2.774000	-0.866000	2.777000
H	3.045000	0.192000	2.817000
H	2.858000	-1.274000	3.791000
C	-2.715000	-0.528000	-2.970000
H	-2.694000	0.565000	-3.015000
H	-2.726000	-0.903000	-4.001000
C	-1.850000	-2.457000	2.563000
H	-2.853000	-2.091000	2.369000
C	-6.232000	-1.740000	-0.830000
C	1.121000	-3.259000	-1.555000
H	2.101000	-3.180000	-1.094000
C	-0.275000	3.550000	-2.490000
H	0.219000	4.229000	-3.182000
C	5.680000	-2.649000	0.146000
C	4.231000	4.346000	-0.341000
H	5.162000	4.460000	-0.888000
C	-6.155000	-1.958000	-2.230000
H	-6.999000	-2.419000	-2.741000
C	2.355000	5.321000	0.832000
H	1.797000	6.179000	1.197000
C	-5.025000	-1.597000	-2.930000
H	-4.953000	-1.762000	-4.004000
C	-0.651000	-4.570000	-2.610000
H	-1.011000	-5.540000	-2.943000
C	0.622000	-4.475000	-2.010000
H	1.223000	-5.373000	-1.897000
C	3.531000	5.472000	0.132000
H	3.927000	6.465000	-0.068000
C	0.834000	-3.316000	3.112000
H	1.849000	-3.648000	3.306000
C	-1.574000	-3.738000	3.030000
H	-2.395000	-4.432000	3.194000
C	4.687000	-2.515000	2.358000
H	4.657000	-2.800000	3.407000
C	-1.465000	5.451000	-1.390000
H	-1.029000	6.165000	-2.084000
C	-2.854000	4.973000	0.569000
H	-3.491000	5.332000	1.373000
C	-7.356000	-2.090000	-0.049000
H	-8.222000	-2.547000	-0.522000
C	6.627000	-3.118000	-0.795000
H	7.361000	-3.862000	-0.498000
C	5.689000	-1.610000	-2.482000
H	5.723000	-1.204000	-3.489000
C	5.621000	-3.061000	1.502000
H	6.335000	-3.798000	1.864000
C	-2.311000	5.862000	-0.363000
H	-2.549000	6.922000	-0.270000
C	-7.322000	-1.838000	1.316000
H	-8.186000	-2.105000	1.925000
C	-6.216000	-1.254000	1.944000
H	-6.224000	-1.068000	3.015000
C	-0.256000	-4.163000	3.297000
H	-0.084000	-5.175000	3.654000
C	6.604000	-2.598000	-2.080000
H	7.334000	-2.954000	-2.806000
H	4.144000	1.252000	-0.963000

Int_4 (3s)

Cu	2.394000	0.048000	-0.484000
Cu	-2.611000	0.656000	0.643000
O	-3.562000	2.388000	0.799000
O	4.159000	-0.003000	-1.716000
O	-3.842000	-0.155000	1.946000
O	4.425000	2.389000	-0.367000
N	1.837000	1.660000	0.793000
N	0.839000	-0.771000	-1.562000
N	-1.561000	1.675000	-0.797000
N	-1.290000	-1.034000	-2.231000

N	-0.937000	-0.468000	1.429000
N	1.125000	-0.978000	2.159000
N	3.759000	-1.061000	0.752000
N	-3.836000	-0.819000	-0.694000
C	-0.320000	-0.158000	-1.773000
C	2.257000	2.970000	0.685000
C	0.690000	1.410000	1.483000
C	-0.552000	1.278000	-1.608000
C	0.286000	0.012000	1.674000
C	3.516000	3.291000	0.072000
C	-3.784000	-1.154000	-1.973000
C	1.464000	4.058000	1.192000
C	-1.892000	3.007000	-0.758000
C	3.594000	-1.436000	2.010000
C	-0.692000	-2.283000	-2.329000
C	0.645000	-2.100000	-1.912000
C	-0.130000	2.425000	2.012000
H	-1.041000	2.155000	2.537000
C	-0.911000	-1.813000	1.776000
C	4.849000	-1.459000	0.050000
C	0.385000	-2.148000	2.226000
C	0.235000	3.741000	1.845000
H	-0.385000	4.546000	2.230000
C	0.226000	2.206000	-2.330000
H	1.047000	1.835000	-2.936000
C	-1.176000	-3.522000	-2.754000
H	-2.208000	-3.659000	-3.060000
C	-4.863000	-0.790000	1.465000
C	-1.188000	4.000000	-1.499000
C	5.005000	-0.878000	-1.282000
C	-2.996000	3.338000	0.099000
C	-4.900000	-1.185000	0.065000
C	2.438000	-0.806000	2.771000
H	2.613000	0.270000	2.852000
H	2.394000	-1.221000	3.786000
C	-2.591000	-0.676000	-2.783000
H	-2.616000	0.414000	-2.858000
H	-2.654000	-1.082000	-3.800000
C	-1.908000	-2.796000	1.735000
H	-2.907000	-2.555000	1.401000
C	-6.004000	-1.927000	-0.471000
C	1.538000	-3.176000	-1.908000
H	2.567000	-3.033000	-1.593000
C	-0.078000	3.554000	-2.278000
H	0.509000	4.275000	-2.840000
C	5.817000	-2.363000	0.599000
C	3.915000	4.626000	-0.017000
H	4.877000	4.822000	-0.482000
C	-5.922000	-2.264000	-1.845000
H	-6.733000	-2.827000	-2.303000
C	1.905000	5.392000	1.070000
H	1.273000	6.188000	1.456000
C	-4.826000	-1.888000	-2.591000
H	-4.752000	-2.144000	-3.645000
C	-0.272000	-4.585000	-2.749000
H	-0.609000	-5.568000	-3.070000
C	1.062000	-4.414000	-2.332000
H	1.734000	-5.268000	-2.342000
C	3.123000	5.670000	0.474000
H	3.468000	6.697000	0.380000
C	0.726000	-3.434000	2.649000
H	1.731000	-3.677000	2.979000
C	-1.573000	-4.081000	2.154000
H	-2.333000	-4.859000	2.131000
C	4.509000	-2.308000	2.646000
H	4.348000	-2.600000	3.681000
C	-1.624000	5.341000	-1.414000
H	-1.098000	6.110000	-1.973000
C	-3.401000	4.685000	0.133000
H	-4.245000	4.954000	0.761000
C	-7.083000	-2.279000	0.373000
H	-7.923000	-2.838000	-0.030000
C	6.917000	-2.765000	-0.194000
H	7.652000	-3.455000	0.211000
C	6.122000	-1.331000	-2.016000
H	6.268000	-0.929000	-3.014000
C	5.594000	-2.780000	1.937000
H	6.300000	-3.466000	2.403000
C	-2.717000	5.657000	-0.614000
H	-3.051000	6.691000	-0.557000
C	-7.042000	-1.896000	1.705000
H	-7.870000	-2.163000	2.358000
C	-5.969000	-1.172000	2.249000
H	-5.967000	-0.889000	3.297000
C	-0.279000	-4.398000	2.606000
H	-0.056000	-5.414000	2.921000
C	7.038000	-2.249000	-1.477000
H	7.886000	-2.554000	-2.089000
H	4.078000	1.539000	-0.734000

Int_5 (3s)

Cu	2.531000	0.313000	-0.666000
Cu	-2.634000	0.702000	0.586000
O	-3.366000	2.536000	0.817000
O	4.281000	0.282000	-1.724000
O	-3.832000	0.020000	1.934000
O	4.672000	2.249000	0.230000
N	1.977000	1.666000	1.100000
N	0.774000	-0.829000	-1.391000
N	-1.592000	1.640000	-0.972000
N	-1.301000	-1.226000	-2.150000
N	-0.931000	-0.380000	1.475000
N	1.120000	-0.994000	2.138000
N	3.722000	-1.058000	0.560000
N	-3.850000	-0.821000	-0.654000
C	-0.375000	-0.286000	-1.760000
C	2.457000	2.947000	1.062000
C	0.762000	1.436000	1.600000
C	-0.692000	1.160000	-1.828000
C	0.309000	0.034000	1.712000
C	3.790000	3.214000	0.584000
C	-3.807000	-1.292000	-1.892000
C	1.656000	4.051000	1.514000
C	-1.962000	2.951000	-1.046000
C	3.543000	-1.554000	1.777000
C	-0.690000	-2.467000	-2.030000
C	0.613000	-2.202000	-1.557000

C	-0.099000	2.469000	2.049000
H	-1.087000	2.231000	2.427000
C	-0.951000	-1.737000	1.774000
C	4.791000	-1.465000	-0.183000
C	0.336000	-2.136000	2.186000
C	0.350000	3.765000	1.985000
H	-0.287000	4.583000	2.309000
C	-0.111000	1.971000	-2.833000
H	0.620000	1.536000	-3.503000
C	-1.138000	-3.761000	-2.309000
H	-2.147000	-3.956000	-2.658000
C	-4.902000	-0.574000	1.484000
C	-1.432000	3.841000	-2.033000
C	5.036000	-0.739000	-1.411000
C	-2.932000	3.384000	-0.068000
C	-4.941000	-1.075000	0.125000
C	2.481000	-0.926000	2.662000
H	2.726000	0.126000	2.815000
H	2.483000	-1.421000	3.639000
C	-2.602000	-0.964000	-2.759000
H	-2.623000	0.094000	-3.032000
H	-2.658000	-1.540000	-3.689000
C	-1.993000	-2.675000	1.737000
H	-2.991000	-2.382000	1.442000
C	-6.074000	-1.809000	-0.355000
C	1.516000	-3.253000	-1.356000
H	2.524000	-3.058000	-1.005000
C	-0.486000	3.292000	-2.935000
H	-0.053000	3.926000	-3.705000
C	5.674000	-2.507000	0.250000
C	4.253000	4.521000	0.602000
H	5.267000	4.694000	0.256000
C	-5.998000	-2.282000	-1.688000
H	-6.831000	-2.846000	-2.101000
C	2.171000	5.370000	1.497000
H	1.544000	6.186000	1.843000
C	-4.875000	-2.038000	-2.447000
H	-4.802000	-2.404000	-3.467000
C	-0.229000	-4.793000	-2.103000
H	-0.533000	-5.816000	-2.306000
C	1.078000	-4.542000	-1.636000
H	1.758000	-5.378000	-1.494000
C	3.455000	5.592000	1.052000
H	3.863000	6.599000	1.039000
C	0.635000	-3.447000	2.569000
H	1.634000	-3.743000	2.871000
C	-1.704000	-3.979000	2.117000
H	-2.495000	-4.723000	2.103000
C	4.382000	-2.568000	2.297000
H	4.205000	-2.949000	3.299000
C	-1.878000	5.182000	-2.053000
H	-1.486000	5.868000	-2.797000
C	-3.340000	4.726000	-0.140000
H	-4.074000	5.079000	0.578000
C	-7.180000	-2.024000	0.500000
H	-8.043000	-2.573000	0.134000
C	6.747000	-2.899000	-0.584000
H	7.412000	-3.698000	-0.266000
C	6.118000	-1.170000	-2.193000
H	6.318000	-0.642000	-3.120000
C	5.415000	-3.059000	1.528000
H	6.056000	-3.852000	1.906000
C	-2.814000	5.592000	-1.115000
H	-3.159000	6.623000	-1.131000
C	-7.139000	-1.522000	1.789000
H	-7.989000	-1.680000	2.449000
C	-6.032000	-0.808000	2.281000
H	-6.023000	-0.431000	3.299000
C	-0.410000	-4.363000	2.526000
H	-0.225000	-5.394000	2.812000
C	6.942000	-2.233000	-1.782000
H	7.771000	-2.525000	-2.423000
H	2.085000	1.577000	-1.502000
H	4.386000	1.644000	-0.504000

Int_6 (2s)

Cu	2.314000	-0.088000	-0.504000
Cu	-2.579000	0.705000	0.589000
O	-3.279000	2.550000	0.896000
O	4.029000	-0.006000	-1.720000
O	-3.750000	-0.023000	1.935000
O	4.373000	2.346000	-0.580000
N	1.881000	1.616000	0.817000
N	0.716000	-0.863000	-1.516000
N	-1.492000	1.705000	-0.893000
N	-1.380000	-1.069000	-2.286000
N	-0.875000	-0.465000	1.389000
N	1.130000	-1.056000	2.207000
N	3.712000	-1.133000	0.738000
N	-3.863000	-0.689000	-0.698000
C	-0.398000	-0.224000	-1.828000
C	2.336000	2.907000	0.725000
C	0.800000	1.360000	1.558000
C	-0.575000	1.238000	-1.741000
C	0.349000	-0.048000	1.688000
C	3.547000	3.220000	0.003000
C	-3.869000	-1.059000	-1.970000
C	1.628000	3.987000	1.368000
C	-1.729000	3.043000	-0.825000
C	3.590000	-1.550000	1.988000
C	-0.844000	-2.351000	-2.270000
C	0.474000	-2.205000	-1.788000
C	0.050000	2.361000	2.219000
H	-0.834000	2.088000	2.784000
C	-0.908000	-1.819000	1.710000
C	4.791000	-1.494000	-0.006000
C	0.350000	-2.203000	2.218000
C	0.461000	3.666000	2.104000
H	-0.099000	4.465000	2.581000
C	0.191000	2.100000	-2.560000
H	0.944000	1.675000	-3.216000
C	-1.369000	-3.592000	-2.638000
H	-2.388000	-3.702000	-2.996000
C	-4.836000	-0.587000	1.486000
C	-1.031000	3.987000	-1.644000
C	4.911000	-0.881000	-1.320000
C	-2.723000	3.449000	0.142000

C	-4.929000	-0.990000	0.098000
C	2.458000	-0.954000	2.810000
H	2.658000	0.108000	2.974000
H	2.414000	-1.437000	3.792000
C	-2.677000	-0.687000	-2.836000
H	-2.657000	0.395000	-2.992000
H	-2.780000	-1.156000	-3.820000
C	-1.937000	-2.764000	1.604000
H	-2.911000	-2.484000	1.226000
C	-6.087000	-1.674000	-0.396000
C	1.312000	-3.319000	-1.660000
H	2.328000	-3.205000	-1.296000
C	-0.042000	3.458000	-2.511000
H	0.533000	4.134000	-3.139000
C	5.785000	-2.398000	0.494000
C	3.960000	4.551000	-0.044000
H	4.878000	4.759000	-0.585000
C	-6.064000	-2.038000	-1.765000
H	-6.919000	-2.559000	-2.190000
C	2.090000	5.320000	1.279000
H	1.527000	6.108000	1.770000
C	-4.967000	-1.743000	-2.544000
H	-4.937000	-2.025000	-3.592000
C	-0.524000	-4.690000	-2.509000
H	-0.891000	-5.676000	-2.782000
C	0.795000	-4.556000	-2.028000
H	1.420000	-5.440000	-1.946000
C	3.247000	5.587000	0.579000
H	3.619000	6.605000	0.504000
C	0.630000	-3.507000	2.635000
H	1.607000	-3.792000	3.011000
C	-1.666000	-4.063000	2.017000
H	-2.448000	-4.814000	1.949000
C	4.531000	-2.429000	2.573000
H	4.403000	-2.754000	3.602000
C	-1.354000	5.357000	-1.529000
H	-0.837000	6.087000	-2.143000
C	-3.010000	4.824000	0.201000
H	-3.763000	5.162000	0.905000
C	-7.162000	-1.946000	0.481000
H	-8.044000	-2.459000	0.108000
C	6.873000	-2.757000	-0.335000
H	7.628000	-3.447000	0.033000
C	6.015000	-1.282000	-2.089000
H	6.131000	-0.844000	-3.076000
C	5.603000	-2.862000	1.822000
H	6.330000	-3.551000	2.247000
C	-2.332000	5.741000	-0.622000
H	-2.585000	6.795000	-0.536000
C	-7.068000	-1.544000	1.803000
H	-7.894000	-1.747000	2.481000
C	-5.938000	-0.875000	2.305000
H	-5.890000	-0.574000	3.347000
C	-0.404000	-4.432000	2.524000
H	-0.233000	-5.459000	2.832000
C	6.961000	-2.200000	-1.601000
H	7.799000	-2.470000	-2.240000
H	4.044000	1.450000	-0.882000

Int_6 (4s)

Cu	2.601000	0.356000	-0.536000
Cu	-2.653000	0.493000	0.694000
O	-3.644000	2.186000	0.988000
O	3.845000	-0.355000	-1.844000
O	-3.840000	-0.441000	1.918000
O	3.874000	2.166000	-0.679000
N	1.684000	1.648000	0.721000
N	0.924000	-0.503000	-1.517000
N	-1.637000	1.718000	-0.711000
N	-1.158000	-0.878000	-2.251000
N	-0.948000	-0.577000	1.461000
N	1.148000	-0.966000	2.170000
N	3.754000	-0.917000	0.783000
N	-3.741000	-0.930000	-0.759000
C	-0.267000	0.034000	-1.746000
C	2.092000	2.968000	0.629000
C	0.588000	1.372000	1.519000
C	-0.631000	1.448000	-1.550000
C	0.240000	-0.029000	1.708000
C	3.228000	3.277000	-0.140000
C	-3.644000	-1.195000	-2.052000
C	1.389000	4.043000	1.254000
C	-2.075000	3.002000	-0.588000
C	3.635000	-1.207000	2.069000
C	-0.489000	-2.091000	-2.346000
C	0.823000	-1.844000	-1.889000
C	-0.146000	2.384000	2.149000
H	-1.007000	2.104000	2.749000
C	-0.838000	-1.923000	1.801000
C	4.824000	-1.374000	0.072000
C	0.479000	-2.183000	2.239000
C	0.226000	3.713000	2.022000
H	-0.341000	4.500000	2.507000
C	0.021000	2.461000	-2.290000
H	0.831000	2.187000	-2.958000
C	-0.905000	-3.346000	-2.797000
H	-1.922000	-3.525000	-3.132000
C	-4.821000	-1.097000	1.369000
C	-1.490000	4.089000	-1.315000
C	4.835000	-1.051000	-1.334000
C	-3.177000	3.200000	0.325000
C	-4.797000	-1.410000	-0.047000
C	2.423000	-0.675000	2.813000
H	2.497000	0.412000	2.909000
H	2.404000	-1.098000	3.824000
C	-2.478000	-0.597000	-2.818000
H	-2.584000	0.489000	-2.862000
H	-2.484000	-0.972000	-3.847000
C	-1.775000	-2.962000	1.760000
H	-2.791000	-2.777000	1.438000
C	-5.839000	-2.187000	-0.651000
C	1.764000	-2.881000	-1.872000
H	2.778000	-2.707000	-1.536000
C	-0.402000	3.768000	-2.168000

H	0.084000	4.559000	-2.733000
C	5.868000	-2.142000	0.671000
C	3.685000	4.577000	-0.312000
H	4.578000	4.766000	-0.903000
C	-5.708000	-2.443000	-2.038000
H	-6.472000	-3.027000	-2.546000
C	1.860000	5.360000	1.072000
H	1.317000	6.175000	1.544000
C	-4.621000	-1.960000	-2.735000
H	-4.510000	-2.152000	-3.798000
C	0.043000	-4.364000	-2.774000
H	-0.237000	-5.358000	-3.111000
C	1.356000	-4.132000	-2.318000
H	2.067000	-4.953000	-2.317000
C	2.985000	5.626000	0.298000
H	3.330000	6.648000	0.169000
C	0.899000	-3.448000	2.652000
H	1.917000	-3.634000	2.983000
C	-1.361000	-4.228000	2.167000
H	-2.073000	-5.048000	2.148000
C	4.621000	-1.968000	2.743000
H	4.495000	-2.189000	3.799000
C	-2.021000	5.386000	-1.147000
H	-1.588000	6.219000	-1.691000
C	-3.674000	4.511000	0.436000
H	-4.511000	4.687000	1.105000
C	-6.915000	-2.647000	0.143000
H	-7.709000	-3.232000	-0.313000
C	6.946000	-2.584000	-0.134000
H	7.747000	-3.167000	0.311000
C	5.916000	-1.525000	-2.084000
H	5.943000	-1.306000	-3.148000
C	5.725000	-2.419000	2.053000
H	6.490000	-3.003000	2.561000
C	-3.096000	5.567000	-0.286000
H	-3.509000	6.566000	-0.162000
C	-6.933000	-2.334000	1.492000
H	-7.760000	-2.682000	2.107000
C	-5.919000	-1.576000	2.102000
H	-5.960000	-1.348000	3.162000
C	-0.048000	-4.470000	2.609000
H	0.236000	-5.471000	2.922000
C	6.950000	-2.270000	-1.481000
H	7.773000	-2.611000	-2.104000
H	4.292000	2.352000	-1.534000

Int_7 (4s)

Cu	-2.506000	0.305000	0.720000
Cu	2.563000	0.616000	-0.599000
O	3.450000	2.366000	-0.795000
O	-3.959000	-0.385000	2.048000
O	3.724000	-0.126000	-1.991000
O	-4.290000	2.614000	0.439000
N	-1.842000	1.828000	-0.853000
N	-0.755000	-0.835000	1.435000
N	1.629000	1.585000	0.982000
N	1.319000	-1.256000	2.183000
N	0.852000	-0.416000	-1.399000
N	-1.224000	-0.838000	-2.127000
N	-3.753000	-0.970000	-0.596000
N	3.810000	-0.930000	0.613000
C	0.399000	-0.305000	1.807000
C	-2.266000	3.135000	-0.846000
C	-0.709000	1.524000	-1.492000
C	0.728000	1.138000	1.856000
C	-0.347000	0.099000	-1.635000
C	-3.501000	3.509000	-0.217000
C	3.813000	-1.374000	1.865000
C	-1.508000	4.166000	-1.506000
C	2.040000	2.883000	1.033000
C	-3.683000	-1.217000	-1.904000
C	0.696000	-2.491000	2.055000
C	-0.606000	-2.212000	1.586000
C	0.125000	2.489000	-2.107000
H	1.046000	2.178000	-2.588000
C	0.774000	-1.760000	-1.754000
C	-4.806000	-1.456000	0.108000
C	-0.528000	-2.037000	-2.217000
C	-0.278000	3.801000	-2.102000
H	0.330000	4.566000	-2.578000
C	0.169000	1.983000	2.843000
H	-0.559000	1.577000	3.535000
C	1.136000	-3.791000	2.318000
H	2.141000	-3.998000	2.673000
C	4.783000	-0.732000	-1.571000
C	1.530000	3.808000	1.997000
C	-4.860000	-1.122000	1.533000
C	3.039000	3.257000	0.065000
C	4.866000	-1.206000	-0.195000
C	-2.545000	-0.605000	-2.697000
H	-2.697000	0.474000	-2.768000
H	-2.551000	-1.008000	-3.715000
C	2.638000	-1.020000	2.764000
H	2.692000	0.039000	3.033000
H	2.705000	-1.593000	3.694000
C	1.738000	-2.777000	-1.724000
H	2.742000	-2.581000	-1.374000
C	6.007000	-1.938000	0.250000
C	-1.511000	-3.256000	1.365000
H	-2.515000	-3.055000	1.011000
C	0.567000	3.303000	2.906000
H	0.150000	3.962000	3.663000
C	-5.835000	-2.244000	-0.482000
C	-3.954000	4.812000	-0.321000
H	-4.901000	5.054000	0.150000
C	5.988000	-2.383000	1.594000
H	6.833000	-2.943000	1.985000
C	-1.998000	5.493000	-1.567000
H	-1.408000	6.249000	-2.076000
C	4.897000	-2.111000	2.393000
H	4.866000	-2.453000	3.424000
C	0.222000	-4.816000	2.097000
H	0.519000	-5.842000	2.289000
C	-1.081000	-4.552000	1.627000
H	-1.763000	-5.382000	1.471000
C	-3.213000	5.801000	-0.998000
H	-3.603000	6.813000	-1.051000

C	-0.914000	-3.301000	-2.671000
H	-1.920000	-3.505000	-3.025000
C	1.360000	-4.037000	-2.172000
H	2.088000	-4.842000	-2.166000
C	-4.663000	-1.980000	-2.574000
H	-4.568000	-2.155000	-3.641000
C	2.024000	5.132000	1.993000
H	1.655000	5.848000	2.720000
C	3.502000	4.580000	0.115000
H	4.264000	4.889000	-0.592000
C	7.075000	-2.181000	-0.651000
H	7.948000	-2.728000	-0.308000
C	-6.899000	-2.728000	0.329000
H	-7.679000	-3.329000	-0.126000
C	-5.948000	-1.645000	2.289000
H	-5.986000	-1.401000	3.345000
C	-5.731000	-2.495000	-1.868000
H	-6.492000	-3.088000	-2.368000
C	2.991000	5.486000	1.062000
H	3.377000	6.502000	1.065000
C	6.996000	-1.713000	-1.956000
H	7.820000	-1.899000	-2.639000
C	5.882000	-1.003000	-2.419000
H	5.831000	-0.646000	-3.442000
C	0.056000	-4.296000	-2.641000
H	-0.196000	-5.295000	-2.985000
C	-6.936000	-2.426000	1.688000
H	-7.755000	-2.802000	2.294000
H	-2.285000	1.527000	1.714000
H	-3.737000	2.104000	1.077000

Int_8 (1s)

Cu	-2.260000	-0.011000	0.512000
Cu	2.353000	0.444000	-0.901000
O	3.069000	2.252000	-1.345000
O	-3.864000	0.191000	1.829000
O	3.639000	-0.586000	-1.963000
O	-2.939000	2.684000	1.686000
N	-1.629000	1.657000	-0.703000
N	-0.678000	-0.908000	1.450000
N	1.551000	1.521000	0.733000
N	1.366000	-1.209000	2.314000
N	0.671000	-0.648000	-1.587000
N	-1.397000	-1.121000	-2.302000
N	-3.860000	-0.886000	-0.665000
N	3.809000	-0.925000	0.750000
C	0.448000	-0.319000	1.811000
C	-2.000000	2.971000	-0.580000
C	-0.906000	1.282000	-1.760000
C	0.731000	1.134000	1.711000
C	-0.527000	-0.155000	-1.859000
C	-2.705000	3.436000	0.587000
C	3.876000	-1.187000	2.048000
C	-1.666000	3.931000	-1.602000
C	1.905000	2.824000	0.633000
C	-3.880000	-1.325000	-1.919000
C	0.772000	-2.466000	2.273000
C	-0.514000	-2.261000	1.733000
C	-0.503000	2.169000	-2.783000
H	0.102000	1.802000	-3.606000
C	0.595000	-2.016000	-1.841000
C	-4.946000	-1.080000	0.130000
C	-0.705000	-2.327000	-2.289000
C	-0.903000	3.482000	-2.706000
H	-0.629000	4.191000	-3.483000
C	0.207000	2.048000	2.650000
H	-0.470000	1.697000	3.420000
C	1.225000	-3.728000	2.665000
H	2.218000	-3.885000	3.074000
C	4.793000	-0.809000	-1.439000
C	1.459000	3.814000	1.556000
C	-4.899000	-0.494000	1.462000
C	2.819000	3.144000	-0.445000
C	4.913000	-1.103000	-0.012000
C	-2.738000	-0.921000	-2.838000
H	-2.836000	0.142000	-3.080000
H	-2.809000	-1.473000	-3.780000
C	2.656000	-0.900000	2.915000
H	2.651000	0.162000	3.182000
H	2.732000	-1.459000	3.853000
C	1.558000	-3.026000	-1.718000
H	2.560000	-2.793000	-1.383000
C	6.165000	-1.521000	0.524000
C	-1.394000	-3.336000	1.568000
H	-2.387000	-3.181000	1.157000
C	0.569000	3.381000	2.567000
H	0.180000	4.097000	3.286000
C	-6.101000	-1.795000	-0.314000
C	-3.065000	4.774000	0.660000
H	-3.594000	5.098000	1.551000
C	6.204000	-1.800000	1.911000
H	7.132000	-2.133000	2.368000
C	-2.065000	5.284000	-1.481000
H	-1.808000	5.983000	-2.271000
C	5.063000	-1.642000	2.670000
H	5.073000	-1.851000	3.736000
C	0.338000	-4.787000	2.498000
H	0.646000	-5.787000	2.789000
C	-0.951000	-4.594000	1.958000
H	-1.611000	-5.450000	1.849000
C	-2.758000	5.691000	-0.364000
H	-3.070000	6.726000	-0.259000
C	-1.092000	-3.625000	-2.633000
H	-2.097000	-3.856000	-2.971000
C	1.178000	-4.320000	-2.057000
H	1.903000	-5.125000	-1.975000
C	-4.974000	-2.052000	-2.440000
H	-4.947000	-2.407000	-3.466000
C	1.964000	5.135000	1.430000
H	1.649000	5.898000	2.136000
C	3.347000	4.452000	-0.469000
H	4.069000	4.703000	-1.239000
C	7.296000	-1.616000	-0.332000
H	8.249000	-1.932000	0.083000
C	-7.193000	-1.969000	0.572000
H	-8.066000	-2.524000	0.241000
C	-6.017000	-0.707000	2.295000

H	-5.992000	-0.282000	3.293000
C	-6.070000	-2.294000	-1.638000
H	-6.920000	-2.855000	-2.019000
C	2.891000	5.424000	0.438000
H	3.287000	6.433000	0.362000
C	7.187000	-1.281000	-1.676000
H	8.063000	-1.345000	-2.315000
C	5.972000	-0.855000	-2.223000
H	5.887000	-0.600000	-3.275000
C	-0.124000	-4.616000	-2.509000
H	-0.378000	-5.640000	-2.764000
C	-7.133000	-1.429000	1.849000
H	-7.974000	-1.563000	2.523000
H	-3.351000	1.792000	1.547000

Int_8 (3s)

Cu	-2.287000	-0.095000	0.515000
Cu	2.552000	0.661000	-0.608000
O	3.238000	2.478000	-1.003000
O	-3.911000	-0.209000	1.795000
O	3.705000	-0.117000	-1.958000
O	-4.236000	2.375000	0.761000
N	-1.838000	1.623000	-0.759000
N	-0.703000	-0.830000	1.550000
N	1.506000	1.702000	0.864000
N	1.388000	-1.043000	2.317000
N	0.836000	-0.512000	-1.388000
N	-1.183000	-1.038000	-2.214000
N	-3.721000	-1.099000	-0.744000
N	3.843000	-0.723000	0.687000
C	0.418000	-0.193000	1.858000
C	-2.274000	2.922000	-0.651000
C	-0.791000	1.357000	-1.548000
C	0.618000	1.266000	1.758000
C	-0.368000	-0.056000	-1.693000
C	-3.439000	3.259000	0.122000
C	3.873000	-1.064000	1.970000
C	-1.587000	3.992000	-1.332000
C	1.770000	3.033000	0.768000
C	-3.657000	-1.423000	-2.032000
C	0.846000	-2.324000	2.307000
C	-0.471000	-2.176000	1.825000
C	-0.066000	2.348000	-2.246000
H	0.788000	2.065000	-2.851000
C	0.830000	-1.866000	-1.714000
C	-4.806000	-1.454000	-0.017000
C	-0.435000	-2.210000	-2.234000
C	-0.460000	3.658000	-2.119000
H	0.083000	4.449000	-2.628000
C	-0.081000	2.153000	2.610000
H	-0.796000	1.753000	3.321000
C	1.370000	-3.565000	2.680000
H	2.387000	-3.675000	3.042000
C	4.789000	-0.672000	-1.513000
C	1.129000	4.003000	1.606000
C	-4.838000	-0.995000	1.366000
C	2.731000	3.404000	-0.243000
C	4.897000	-1.043000	-0.113000
C	-2.490000	-0.876000	-2.839000
H	-2.649000	0.194000	-3.006000
H	-2.460000	-1.357000	-3.822000
C	2.697000	-0.669000	2.850000
H	2.691000	0.414000	2.996000
H	2.805000	-1.131000	3.836000
C	1.831000	-2.840000	-1.603000
H	2.808000	-2.590000	-1.211000
C	6.059000	-1.714000	0.376000
C	-1.309000	-3.290000	1.701000
H	-2.325000	-3.184000	1.336000
C	0.179000	3.506000	2.532000
H	-0.342000	4.200000	3.187000
C	-5.874000	-2.222000	-0.556000
C	-3.846000	4.584000	0.189000
H	-4.734000	4.802000	0.774000
C	6.065000	-2.048000	1.752000
H	6.927000	-2.557000	2.176000
C	-2.036000	5.329000	-1.227000
H	-1.493000	6.109000	-1.751000
C	4.979000	-1.733000	2.542000
H	4.969000	-1.987000	3.598000
C	0.524000	-4.662000	2.553000
H	0.888000	-5.646000	2.832000
C	-0.794000	-4.527000	2.072000
H	-1.420000	-5.411000	1.992000
C	-3.155000	5.612000	-0.476000
H	-3.515000	6.633000	-0.391000
C	-0.747000	-3.502000	-2.664000
H	-1.724000	-3.759000	-3.062000
C	1.527000	-4.127000	-2.027000
H	2.285000	-4.902000	-1.959000
C	-4.672000	-2.179000	-2.656000
H	-4.584000	-2.438000	-3.707000
C	1.475000	5.364000	1.453000
H	1.008000	6.114000	2.084000
C	3.040000	4.769000	-0.340000
H	3.772000	5.082000	-1.079000
C	7.121000	-2.006000	-0.516000
H	8.009000	-2.508000	-0.144000
C	-6.956000	-2.589000	0.293000
H	-7.768000	-3.188000	-0.109000
C	-5.924000	-1.420000	2.167000
H	-5.948000	-1.100000	3.204000
C	-5.770000	-2.584000	-1.919000
H	-6.556000	-3.176000	-2.382000
C	2.418000	5.713000	0.497000
H	2.691000	6.760000	0.385000
C	7.014000	-1.637000	-1.849000
H	7.832000	-1.857000	-2.529000
C	5.880000	-0.981000	-2.349000
H	5.814000	-0.700000	-3.395000
C	0.260000	-4.455000	-2.552000
H	0.065000	-5.474000	-2.874000
C	-6.960000	-2.192000	1.625000
H	-7.790000	-2.482000	2.262000
H	-3.844000	1.501000	0.955000

Int_9 (4s)

Cu	3.475000	-0.224000	0.549000
Cu	-2.117000	-1.225000	-0.124000
O	-1.695000	-3.114000	0.353000
O	4.716000	0.892000	1.674000
O	-2.578000	-1.721000	-1.954000
O	4.912000	-1.713000	0.320000
N	2.432000	-1.603000	-0.693000
N	-1.482000	2.658000	2.209000
N	-1.415000	-0.887000	1.836000
N	-3.381000	1.469000	1.900000
N	-0.605000	0.164000	-1.038000
N	1.279000	0.884000	-2.025000
N	4.032000	1.442000	-0.911000
N	-4.220000	-0.600000	-0.141000
C	-2.018000	1.457000	2.187000
C	3.043000	-2.808000	-0.638000
C	1.217000	-1.504000	-1.243000
C	-1.266000	0.239000	2.540000
C	0.627000	-0.158000	-1.393000
C	4.384000	-2.816000	-0.056000
C	-5.002000	-0.070000	0.790000
C	2.428000	-4.001000	-1.109000
C	-0.788000	-2.028000	2.258000
C	3.634000	1.729000	-2.143000
C	-3.720000	2.805000	1.724000
C	-2.517000	3.525000	1.915000
C	0.519000	-2.636000	-1.723000
H	-0.479000	-2.516000	-2.133000
C	-0.798000	1.471000	-1.458000
C	4.976000	2.195000	-0.311000
C	0.379000	1.941000	-2.077000
C	1.123000	-3.875000	-1.644000
H	0.598000	-4.758000	-1.997000
C	-0.416000	0.300000	3.673000
H	-0.298000	1.253000	4.175000
C	-4.932000	3.438000	1.433000
H	-5.851000	2.883000	1.277000
C	-3.845000	-1.641000	-2.253000
C	0.032000	-2.066000	3.428000
C	5.329000	1.835000	1.065000
C	-0.999000	-3.206000	1.449000
C	-4.761000	-1.043000	-1.311000
C	2.553000	0.847000	-2.744000
H	2.896000	-0.190000	-2.750000
H	2.364000	1.146000	-3.781000
C	-4.345000	0.387000	2.079000
H	-3.818000	-0.453000	2.537000
H	-5.114000	0.726000	2.782000
C	-1.929000	2.291000	-1.376000
H	-2.839000	1.934000	-0.908000
C	-6.160000	-0.945000	-1.594000
C	-2.510000	4.922000	1.803000
H	-1.587000	5.475000	1.943000
C	0.220000	-0.836000	4.108000
H	0.868000	-0.804000	4.981000
C	5.612000	3.291000	-0.966000
C	5.034000	-4.074000	0.029000
H	6.028000	-4.102000	0.465000
C	-6.968000	-0.382000	-0.576000
H	-8.040000	-0.295000	-0.734000
C	3.143000	-5.223000	-1.006000
H	2.681000	-6.142000	-1.356000
C	-6.399000	0.045000	0.605000
H	-7.011000	0.469000	1.397000
C	-4.905000	4.828000	1.333000
H	-5.825000	5.360000	1.107000
C	-3.712000	5.559000	1.514000
H	-3.738000	6.642000	1.425000
C	4.418000	-5.236000	-0.448000
H	4.952000	-6.181000	-0.374000
C	0.471000	3.224000	-2.624000
H	1.381000	3.587000	-3.089000
C	-1.844000	3.568000	-1.918000
H	-2.704000	4.228000	-1.861000
C	4.212000	2.788000	-2.878000
H	3.883000	2.986000	-3.894000
C	0.609000	-3.292000	3.828000
H	1.237000	-3.327000	4.713000
C	-0.421000	-4.400000	1.907000
H	-0.588000	-5.304000	1.329000
C	-6.650000	-1.418000	-2.834000
H	-7.711000	-1.348000	-3.056000
C	6.614000	4.025000	-0.280000
H	7.108000	4.852000	-0.783000
C	6.351000	2.602000	1.683000
H	6.630000	2.341000	2.699000
C	5.196000	3.560000	-2.293000
H	5.655000	4.379000	-2.841000
C	0.365000	-4.428000	3.073000
H	0.802000	-5.375000	3.382000
C	-5.761000	-1.977000	-3.736000
H	-6.133000	-2.347000	-4.689000
C	-4.386000	-2.099000	-3.461000
H	-3.716000	-2.552000	-4.185000
C	-0.661000	4.028000	-2.531000
H	-0.631000	5.034000	-2.939000
C	6.962000	3.670000	1.018000
H	7.734000	4.236000	1.533000
H	2.147000	0.288000	1.284000

Int_10 (3s)

Cu	3.795000	1.441000	-0.723000
Cu	-2.699000	0.190000	0.653000
O	-3.991000	1.673000	0.904000
O	4.599000	-0.091000	-1.641000
O	-3.677000	-0.862000	1.994000
O	2.939000	3.135000	-1.096000
N	1.270000	2.073000	0.847000
N	0.896000	-0.210000	-1.996000
N	-1.960000	1.512000	-0.827000
N	-1.194000	-1.017000	-2.330000
N	-0.832000	-0.595000	1.352000

N	1.238000	-0.721000	2.201000
N	3.997000	-0.713000	0.964000
N	-3.664000	-1.422000	-0.665000
C	-0.386000	0.064000	-1.971000
C	1.349000	3.414000	0.695000
C	0.353000	1.569000	1.661000
C	-0.933000	1.397000	-1.672000
C	0.246000	0.092000	1.722000
C	2.267000	3.921000	-0.322000
C	-3.590000	-1.712000	-1.953000
C	0.520000	4.320000	1.447000
C	-2.557000	2.729000	-0.659000
C	3.725000	-0.966000	2.231000
C	-0.319000	-2.061000	-2.602000
C	0.977000	-1.537000	-2.380000
C	-0.534000	2.369000	2.427000
H	-1.275000	1.901000	3.069000
C	-0.540000	-1.932000	1.604000
C	5.055000	-1.313000	0.374000
C	0.762000	-2.025000	2.142000
C	-0.424000	3.737000	2.331000
H	-1.079000	4.385000	2.909000
C	-0.382000	2.525000	-2.329000
H	0.507000	2.387000	-2.934000
C	-0.525000	-3.372000	-3.039000
H	-1.520000	-3.776000	-3.199000
C	-4.571000	-1.679000	1.531000
C	-2.115000	3.902000	-1.342000
C	5.316000	-0.973000	-1.020000
C	-3.671000	2.756000	0.259000
C	-4.589000	-2.033000	0.122000
C	2.500000	-0.288000	2.816000
H	2.571000	0.789000	2.661000
H	2.439000	-0.485000	3.894000
C	-2.577000	-0.955000	-2.794000
H	-2.863000	0.099000	-2.824000
H	-2.607000	-1.335000	-3.823000
C	-1.304000	-3.090000	1.412000
H	-2.301000	-3.033000	0.999000
C	-5.527000	-2.983000	-0.396000
C	2.112000	-2.332000	-2.583000
H	3.096000	-1.909000	-2.412000
C	-0.967000	3.758000	-2.163000
H	-0.549000	4.633000	-2.654000
C	5.898000	-2.246000	1.069000
C	2.334000	5.323000	-0.458000
H	3.019000	5.718000	-1.204000
C	-5.427000	-3.267000	-1.781000
H	-6.113000	-3.985000	-2.226000
C	0.645000	5.716000	1.259000
H	0.020000	6.394000	1.835000
C	-4.469000	-2.647000	-2.553000
H	-4.381000	-2.863000	-3.614000
C	0.614000	-4.150000	-3.239000
H	0.499000	-5.180000	-3.571000
C	1.910000	-3.640000	-3.015000
H	2.769000	-4.285000	-3.181000
C	1.547000	6.187000	0.318000
H	1.644000	7.261000	0.165000
C	1.328000	-3.248000	2.514000
H	2.333000	-3.313000	2.912000
C	-0.744000	-4.308000	1.778000
H	-1.320000	-5.220000	1.640000
C	4.532000	-1.820000	3.025000
H	4.293000	-1.975000	4.075000
C	-2.817000	5.114000	-1.147000
H	-2.484000	6.015000	-1.655000
C	-4.346000	3.981000	0.393000
H	-5.201000	4.024000	1.061000
C	-6.471000	-3.576000	0.476000
H	-7.188000	-4.294000	0.087000
C	6.955000	-2.891000	0.383000
H	7.587000	-3.601000	0.912000
C	6.367000	-1.669000	-1.648000
H	6.565000	-1.444000	-2.692000
C	5.605000	-2.456000	2.440000
H	6.234000	-3.128000	3.021000
C	-3.913000	5.127000	-0.299000
H	-4.457000	6.057000	-0.151000
C	-6.456000	-3.222000	1.816000
H	-7.181000	-3.674000	2.491000
C	-5.538000	-2.299000	2.343000
H	-5.549000	-2.049000	3.400000
C	0.552000	-4.387000	2.324000
H	0.960000	-5.357000	2.595000
C	7.158000	-2.600000	-0.955000
H	7.966000	-3.098000	-1.491000
H	4.963000	1.954000	0.249000

TS-1

Cu	-2.459000	0.237000	0.412000
Cu	2.733000	0.534000	-0.645000
O	3.646000	2.277000	-0.922000
O	-4.093000	-0.441000	2.003000
O	3.892000	-0.328000	-1.933000
O	-3.903000	2.123000	0.489000
N	-1.635000	1.725000	-0.902000
N	-0.868000	-0.595000	1.524000
N	1.683000	1.677000	0.795000
N	1.229000	-1.006000	2.224000
N	0.980000	-0.474000	-1.516000
N	-1.125000	-0.895000	-2.176000
N	-3.787000	-0.980000	-0.706000
N	3.809000	-0.953000	0.707000
C	0.327000	-0.077000	1.752000
C	-2.045000	2.998000	-0.698000
C	-0.554000	1.482000	-1.640000
C	0.676000	1.348000	1.606000
C	-0.204000	0.055000	-1.784000
C	-3.255000	3.178000	0.095000
C	3.716000	-1.288000	1.985000
C	-1.337000	4.114000	-1.247000
C	2.083000	2.978000	0.716000
C	-3.641000	-1.249000	-1.996000
C	0.549000	-2.214000	2.303000
C	-0.764000	-1.942000	1.864000
C	0.208000	2.516000	-2.233000

H	1.088000	2.275000	-2.820000
C	0.857000	-1.839000	-1.764000
C	-4.934000	-1.356000	-0.063000
C	-0.463000	-2.116000	-2.177000
C	-0.188000	3.821000	-2.028000
H	0.385000	4.639000	-2.458000
C	-0.020000	2.319000	2.367000
H	-0.849000	2.003000	2.991000
C	0.949000	-3.484000	2.727000
H	1.965000	-3.687000	3.050000
C	4.882000	-1.009000	-1.428000
C	1.467000	4.019000	1.483000
C	-5.097000	-1.023000	1.332000
C	3.164000	3.246000	-0.206000
C	4.864000	-1.395000	-0.033000
C	-2.448000	-0.669000	-2.751000
H	-2.587000	0.412000	-2.830000
H	-2.444000	-1.078000	-3.768000
C	2.550000	-0.740000	2.789000
H	2.650000	0.344000	2.885000
H	2.574000	-1.162000	3.800000
C	1.793000	-2.877000	-1.672000
H	2.812000	-2.678000	-1.371000
C	5.908000	-2.202000	0.525000
C	-1.724000	-2.961000	1.839000
H	-2.736000	-2.752000	1.515000
C	0.379000	3.636000	2.306000
H	-0.140000	4.393000	2.890000
C	-5.986000	-2.051000	-0.743000
C	-3.656000	4.505000	0.330000
H	-4.547000	4.670000	0.927000
C	5.782000	-2.531000	1.897000
H	6.548000	-3.141000	2.370000
C	-1.802000	5.423000	-0.976000
H	-1.265000	6.278000	-1.378000
C	4.697000	-2.086000	2.620000
H	4.589000	-2.335000	3.672000
C	-0.017000	-4.485000	2.698000
H	0.250000	-5.489000	3.016000
C	-1.333000	-4.226000	2.262000
H	-2.056000	-5.036000	2.259000
C	-2.935000	5.592000	-0.194000
H	-3.287000	6.599000	0.016000
C	-0.894000	-3.402000	-2.513000
H	-1.914000	-3.602000	-2.823000
C	1.371000	-4.160000	-2.002000
H	2.078000	-4.982000	-1.944000
C	-4.619000	-1.959000	-2.734000
H	-4.451000	-2.171000	-3.786000
C	1.958000	5.338000	1.364000
H	1.501000	6.136000	1.940000
C	3.617000	4.575000	-0.270000
H	4.438000	4.804000	-0.942000
C	6.981000	-2.617000	-0.298000
H	7.778000	-3.224000	0.123000
C	-7.177000	-2.389000	-0.052000
H	-7.967000	-2.914000	-0.583000
C	-6.291000	-1.362000	1.960000
H	-6.407000	-1.102000	3.007000
C	-5.779000	-2.357000	-2.110000
H	-6.547000	-2.897000	-2.657000
C	3.018000	5.584000	0.502000
H	3.399000	6.599000	0.413000
C	6.994000	-2.231000	-1.628000
H	7.820000	-2.544000	-2.263000
C	5.977000	-1.441000	-2.191000
H	6.013000	-1.156000	-3.238000
C	0.049000	-4.421000	-2.417000
H	-0.241000	-5.438000	-2.665000
C	-7.321000	-2.037000	1.273000
H	-8.236000	-2.286000	1.804000
H	-4.256000	0.707000	2.221000
H	-4.248000	1.734000	2.157000

TS-1

Cu	-2.456000	-0.029000	0.757000
Cu	2.736000	0.783000	-0.622000
O	3.221000	2.784000	-0.920000
O	-4.344000	0.212000	1.640000
O	4.077000	-0.041000	-1.906000
O	-4.808000	2.106000	-0.219000
N	-2.072000	1.566000	-0.978000
N	-0.668000	-0.851000	1.309000
N	1.508000	1.782000	0.912000
N	1.391000	-1.053000	2.148000
N	0.896000	-0.347000	-1.591000
N	-1.167000	-1.076000	-2.126000
N	-3.740000	-1.219000	-0.580000
N	3.991000	-0.680000	0.742000
C	0.420000	-0.197000	1.711000
C	-2.570000	2.846000	-0.927000
C	-0.874000	1.370000	-1.540000
C	0.577000	1.270000	1.717000
C	-0.374000	-0.007000	-1.727000
C	-3.921000	3.090000	-0.495000
C	3.901000	-1.065000	2.007000
C	-1.784000	3.973000	-1.350000
C	1.706000	3.120000	0.883000
C	-3.572000	-1.713000	-1.797000
C	0.891000	-2.343000	2.029000
C	-0.413000	-2.205000	1.511000
C	-0.042000	2.426000	-1.990000
H	0.937000	2.202000	-2.396000
C	0.969000	-1.693000	-1.921000
C	-4.789000	-1.629000	0.179000
C	-0.316000	-2.166000	-2.257000
C	-0.488000	3.716000	-1.859000
H	0.142000	4.549000	-2.158000
C	-0.222000	2.081000	2.559000
H	-0.975000	1.616000	3.190000
C	1.441000	-3.590000	2.339000
H	2.453000	-3.689000	2.717000
C	5.125000	-0.557000	-1.370000
C	0.977000	4.024000	1.734000

C	-5.023000	-0.905000	1.404000
C	2.675000	3.602000	-0.099000
C	5.108000	-0.976000	0.031000
C	-2.519000	-1.052000	-2.670000
H	-2.804000	-0.008000	-2.814000
H	-2.497000	-1.537000	-3.652000
C	2.657000	-0.675000	2.784000
H	2.625000	0.408000	2.922000
H	2.681000	-1.138000	3.776000
C	2.075000	-2.552000	-1.982000
H	3.063000	-2.173000	-1.762000
C	6.231000	-1.656000	0.611000
C	-1.213000	-3.332000	1.294000
H	-2.218000	-3.235000	0.896000
C	-0.013000	3.443000	2.568000
H	-0.606000	4.084000	3.216000
C	-5.655000	-2.690000	-0.221000
C	-4.400000	4.391000	-0.474000
H	-5.428000	4.537000	-0.159000
C	6.100000	-2.047000	1.967000
H	6.921000	-2.570000	2.452000
C	-2.309000	5.287000	-1.290000
H	-1.683000	6.117000	-1.602000
C	4.944000	-1.764000	2.660000
H	4.831000	-2.058000	3.700000
C	0.633000	-4.702000	2.121000
H	1.021000	-5.691000	2.347000
C	-0.673000	-4.575000	1.609000
H	-1.270000	-5.469000	1.453000
C	-3.601000	5.486000	-0.858000
H	-4.018000	6.488000	-0.816000
C	-0.551000	-3.484000	-2.659000
H	-1.544000	-3.844000	-2.911000
C	1.848000	-3.865000	-2.377000
H	2.686000	-4.553000	-2.442000
C	-4.408000	-2.740000	-2.298000
H	-4.243000	-3.126000	-3.300000
C	1.258000	5.404000	1.675000
H	0.723000	6.093000	2.321000
C	2.917000	4.997000	-0.085000
H	3.651000	5.389000	-0.783000
C	7.384000	-1.896000	-0.171000
H	8.237000	-2.405000	0.270000
C	-6.686000	-3.103000	0.662000
H	-7.339000	-3.922000	0.376000
C	-6.030000	-1.367000	2.251000
H	-6.205000	-0.840000	3.184000
C	-5.416000	-3.245000	-1.503000
H	-6.047000	-4.054000	-1.860000
C	2.223000	5.854000	0.779000
H	2.445000	6.919000	0.738000
C	7.408000	-1.460000	-1.489000
H	8.299000	-1.636000	-2.088000
C	6.322000	-0.801000	-2.080000
H	6.365000	-0.480000	-3.117000
C	0.556000	-4.326000	-2.709000
H	0.422000	-5.360000	-3.013000
C	-6.847000	-2.454000	1.873000
H	-7.636000	-2.772000	2.548000
H	-2.616000	0.268000	2.287000
H	-4.478000	1.409000	0.396000

TS-2

Cu	-2.696000	0.303000	0.698000
Cu	2.665000	0.587000	-0.590000
O	3.490000	2.373000	-0.915000
O	-3.813000	-0.655000	2.006000
O	3.752000	-0.214000	-1.968000
O	-4.169000	2.554000	0.648000
N	-1.825000	1.811000	-0.733000
N	-0.744000	-0.706000	1.492000
N	1.685000	1.660000	0.918000
N	1.338000	-1.114000	2.234000
N	0.857000	-0.427000	-1.361000
N	-1.216000	-0.809000	-2.127000
N	-3.762000	-0.976000	-0.659000
N	3.834000	-0.927000	0.648000
C	0.419000	-0.175000	1.820000
C	-2.258000	3.114000	-0.711000
C	-0.703000	1.516000	-1.402000
C	0.753000	1.265000	1.785000
C	-0.337000	0.100000	-1.587000
C	-3.498000	3.450000	-0.032000
C	3.816000	-1.316000	1.914000
C	-1.522000	4.157000	-1.381000
C	2.069000	2.966000	0.884000
C	-3.679000	-1.160000	-1.970000
C	0.704000	-2.346000	2.168000
C	-0.603000	-2.074000	1.705000
C	0.106000	2.493000	-2.029000
H	1.023000	2.191000	-2.523000
C	0.770000	-1.757000	-1.761000
C	-4.791000	-1.542000	0.037000
C	-0.532000	-2.011000	-2.243000
C	-0.302000	3.803000	-2.005000
H	0.295000	4.576000	-2.483000
C	0.138000	2.172000	2.680000
H	-0.622000	1.807000	3.360000
C	1.139000	-3.637000	2.478000
H	2.149000	-3.836000	2.820000
C	4.792000	-0.876000	-1.542000
C	1.517000	3.949000	1.766000
C	-4.789000	-1.324000	1.464000
C	3.063000	3.299000	-0.111000
C	4.863000	-1.306000	-0.161000
C	-2.522000	-0.529000	-2.716000
H	-2.648000	0.555000	-2.748000
H	-2.511000	-0.893000	-3.749000
C	2.662000	-0.863000	2.793000
H	2.739000	0.211000	2.980000
H	2.723000	-1.368000	3.764000
C	1.723000	-2.784000	-1.750000
H	2.726000	-2.604000	-1.388000
C	5.962000	-2.093000	0.312000
C	-1.520000	-3.120000	1.543000
H	-2.529000	-2.922000	1.206000
C	0.522000	3.496000	2.669000

H	0.063000	4.204000	3.355000
C	-5.817000	-2.312000	-0.597000
C	-3.946000	4.776000	-0.119000
H	-4.881000	5.012000	0.378000
C	5.920000	-2.474000	1.676000
H	6.731000	-3.071000	2.087000
C	-2.021000	5.478000	-1.414000
H	-1.452000	6.244000	-1.933000
C	4.857000	-2.099000	2.469000
H	4.811000	-2.394000	3.513000
C	0.215000	-4.664000	2.308000
H	0.509000	-5.685000	2.534000
C	-1.093000	-4.408000	1.849000
H	-1.785000	-5.237000	1.736000
C	-3.227000	5.767000	-0.803000
H	-3.621000	6.780000	-0.837000
C	-0.926000	-3.259000	-2.732000
H	-1.933000	-3.443000	-3.091000
C	1.337000	-4.029000	-2.232000
H	2.058000	-4.841000	-2.239000
C	-4.652000	-1.902000	-2.679000
H	-4.553000	-2.021000	-3.754000
C	1.983000	5.280000	1.681000
H	1.577000	6.037000	2.344000
C	3.492000	4.636000	-0.142000
H	4.246000	4.917000	-0.869000
C	7.002000	-2.444000	-0.581000
H	7.840000	-3.035000	-0.225000
C	-6.854000	-2.864000	0.191000
H	-7.640000	-3.443000	-0.285000
C	-5.845000	-1.889000	2.194000
H	-5.866000	-1.734000	3.268000
C	-5.711000	-2.465000	-2.000000
H	-6.468000	-3.035000	-2.534000
C	2.954000	5.591000	0.740000
H	3.315000	6.615000	0.674000
C	6.929000	-2.016000	-1.896000
H	7.728000	-2.279000	-2.585000
C	5.855000	-1.246000	-2.377000
H	5.823000	-0.928000	-3.415000
C	0.035000	-4.265000	-2.718000
H	-0.226000	-5.254000	-3.084000
C	-6.847000	-2.644000	1.558000
H	-7.645000	-3.063000	2.167000
H	-2.630000	1.570000	1.932000
H	-3.310000	1.991000	1.483000

TS-3

Cu	-2.459000	0.237000	0.412000
Cu	2.733000	0.534000	-0.645000
O	3.646000	2.277000	-0.922000
O	-4.093000	-0.441000	2.003000
O	3.892000	-0.328000	-1.933000
O	-3.903000	2.123000	0.489000
N	-1.635000	1.725000	-0.902000
N	-0.868000	-0.595000	1.524000
N	1.683000	1.677000	0.795000
N	1.229000	-1.006000	2.224000
N	0.980000	-0.474000	-1.516000
N	-1.125000	-0.895000	-2.176000
N	-3.787000	-0.980000	-0.706000
N	3.809000	-0.953000	0.707000
C	0.327000	-0.077000	1.752000
C	-2.045000	2.998000	-0.698000
C	-0.554000	1.482000	-1.640000
C	0.676000	1.348000	1.606000
C	-0.204000	0.055000	-1.784000
C	-3.255000	3.178000	0.095000
C	3.716000	-1.288000	1.985000
C	-1.337000	4.114000	-1.247000
C	2.083000	2.978000	0.716000
C	-3.641000	-1.249000	-1.996000
C	0.549000	-2.214000	2.303000
C	-0.764000	-1.942000	1.864000
C	0.208000	2.516000	-2.233000
H	1.088000	2.275000	-2.820000
C	0.857000	-1.839000	-1.764000
C	-4.934000	-1.356000	-0.063000
C	-0.463000	-2.116000	-2.177000
C	-0.188000	3.821000	-2.028000
H	0.385000	4.639000	-2.458000
C	-0.020000	2.319000	2.367000
H	-0.849000	2.003000	2.991000
C	0.949000	-3.484000	2.727000
H	1.965000	-3.687000	3.050000
C	4.882000	-1.009000	-1.428000
C	1.467000	4.019000	1.483000
C	-5.097000	-1.023000	1.332000
C	3.164000	3.246000	-0.206000
C	4.864000	-1.395000	-0.033000
C	-2.448000	-0.669000	-2.751000
H	-2.587000	0.412000	-2.830000
H	-2.444000	-1.078000	-3.768000
C	2.550000	-0.740000	2.789000
H	2.650000	0.344000	2.885000
H	2.574000	-1.162000	3.800000
C	1.793000	-2.877000	-1.672000
H	2.812000	-2.678000	-1.371000
C	5.908000	-2.202000	0.525000
C	-1.724000	-2.961000	1.839000
H	-2.736000	-2.752000	1.515000
C	0.379000	3.636000	2.306000
H	-0.140000	4.393000	2.890000
C	-5.986000	-2.051000	-0.743000
C	-3.656000	4.505000	0.330000
H	-4.547000	4.670000	0.927000
C	5.782000	-2.531000	1.897000
H	6.548000	-3.141000	2.370000
C	-1.802000	5.423000	-0.976000
H	-1.265000	6.278000	-1.378000
C	4.697000	-2.086000	2.620000
H	4.589000	-2.335000	3.672000
C	-0.017000	-4.485000	2.698000
H	0.250000	-5.489000	3.016000
C	-1.333000	-4.226000	2.262000
H	-2.056000	-5.036000	2.259000
C	-2.935000	5.592000	-0.194000
H	-3.287000	6.599000	0.016000
C	-0.894000	-3.402000	-2.513000

H	-1.914000	-3.602000	-2.823000
C	1.371000	-4.160000	-2.002000
H	2.078000	-4.982000	-1.944000
C	-4.619000	-1.959000	-2.734000
H	-4.451000	-2.171000	-3.786000
C	1.958000	5.338000	1.364000
H	1.501000	6.136000	1.940000
C	3.617000	4.575000	-0.270000
H	4.438000	4.804000	-0.942000
C	6.981000	-2.617000	-0.298000
H	7.778000	-3.224000	0.123000
C	-7.177000	-2.389000	-0.052000
H	-7.967000	-2.914000	-0.583000
C	-6.291000	-1.362000	1.960000
H	-6.407000	-1.102000	3.007000
C	-5.779000	-2.357000	-2.110000
H	-6.547000	-2.897000	-2.657000
C	3.018000	5.584000	0.502000
H	3.399000	6.599000	0.413000
C	6.994000	-2.231000	-1.628000
H	7.820000	-2.544000	-2.263000
C	5.977000	-1.441000	-2.191000
H	6.013000	-1.156000	-3.238000
C	0.049000	-4.421000	-2.417000
H	-0.241000	-5.438000	-2.665000
C	-7.321000	-2.037000	1.273000
H	-8.236000	-2.286000	1.804000
H	-4.256000	0.707000	2.221000
H	-4.248000	1.734000	2.157000

Int-7

Cu	2.333000	0.223000	-0.387000
Cu	-2.746000	0.496000	0.568000
O	-3.462000	2.299000	1.003000
O	4.126000	-0.355000	-1.964000
O	-3.839000	-0.348000	1.901000
O	3.653000	2.459000	-0.820000
N	1.598000	1.867000	0.803000
N	0.853000	-0.654000	-1.535000
N	-1.660000	1.634000	-0.864000
N	-1.219000	-1.093000	-2.276000
N	-0.893000	-0.438000	1.532000
N	1.225000	-0.773000	2.208000
N	3.835000	-0.854000	0.696000
N	-3.775000	-1.028000	-0.714000
C	-0.341000	-0.146000	-1.820000
C	1.929000	3.179000	0.634000
C	0.565000	1.566000	1.592000
C	-0.702000	1.282000	-1.724000
C	0.273000	0.129000	1.768000
C	3.027000	3.511000	-0.216000
C	-3.694000	-1.396000	-1.987000
C	1.209000	4.237000	1.274000
C	-2.032000	2.941000	-0.775000
C	3.719000	-1.075000	2.002000
C	-0.540000	-2.306000	-2.285000
C	0.759000	-2.017000	-1.817000
C	-0.223000	2.543000	2.245000
H	-1.072000	2.234000	2.843000
C	-0.734000	-1.784000	1.849000
C	4.934000	-1.349000	0.041000
C	0.591000	-2.009000	2.278000
C	0.104000	3.870000	2.083000
H	-0.483000	4.645000	2.568000
C	-0.062000	2.228000	-2.561000
H	0.707000	1.890000	-3.247000
C	-0.932000	-3.593000	-2.663000
H	-1.938000	-3.808000	-3.009000
C	-4.829000	-1.060000	1.430000
C	-1.460000	3.963000	-1.605000
C	5.088000	-1.117000	-1.361000
C	-3.026000	3.245000	0.232000
C	-4.812000	-1.482000	0.050000
C	2.541000	-0.473000	2.758000
H	2.654000	0.613000	2.778000
H	2.568000	-0.826000	3.794000
C	-2.553000	-0.853000	-2.827000
H	-2.662000	0.227000	-2.950000
H	-2.589000	-1.302000	-3.825000
C	-1.651000	-2.844000	1.813000
H	-2.674000	-2.677000	1.505000
C	-5.843000	-2.327000	-0.475000
C	1.710000	-3.038000	-1.710000
H	2.709000	-2.831000	-1.342000
C	-0.450000	3.549000	-2.508000
H	0.016000	4.285000	-3.159000
C	5.949000	-2.106000	0.708000
C	3.395000	4.828000	-0.391000
H	4.236000	5.075000	-1.034000
C	-5.730000	-2.684000	-1.840000
H	-6.489000	-3.320000	-2.290000
C	1.608000	5.583000	1.072000
H	1.055000	6.378000	1.562000
C	-4.665000	-2.230000	-2.588000
H	-4.569000	-2.498000	-3.636000
C	0.027000	-4.594000	-2.558000
H	-0.233000	-5.610000	-2.838000
C	1.328000	-4.321000	-2.087000
H	2.045000	-5.134000	-2.016000
C	2.682000	5.864000	0.259000
H	2.995000	6.892000	0.102000
C	1.046000	-3.266000	2.687000
H	2.066000	-3.432000	3.019000
C	-1.203000	-4.096000	2.214000
H	-1.893000	-4.935000	2.206000
C	4.687000	-1.799000	2.740000
H	4.546000	-1.946000	3.806000
C	-1.914000	5.291000	-1.466000
H	-1.500000	6.072000	-2.096000
C	-3.439000	4.586000	0.318000
H	-4.195000	4.842000	1.054000
C	-6.897000	-2.743000	0.371000
H	-7.685000	-3.376000	-0.025000
C	7.053000	-2.623000	-0.018000
H	7.809000	-3.197000	0.509000
C	6.168000	-1.637000	-2.045000
H	6.267000	-1.452000	-3.112000
C	5.789000	-2.312000	2.099000
H	6.538000	-2.878000	2.645000

C	-2.892000	5.571000	-0.520000
H	-3.247000	6.594000	-0.416000
C	-6.910000	-2.317000	1.688000
H	-7.723000	-2.628000	2.339000
C	-5.906000	-1.485000	2.217000
H	-5.941000	-1.166000	3.254000
C	0.123000	-4.306000	2.646000
H	0.430000	-5.300000	2.955000
C	7.151000	-2.396000	-1.371000
H	7.990000	-2.791000	-1.935000
H	4.182000	-0.443000	-2.929000
H	4.390000	2.777000	-1.365000