Reactivity and Mechanism of Photo- and Electrocatalytic Hydrogen Evolution by a Diimine Copper(I) Complex

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Supporting Information

Table S1. Crystallographic data for complex $[1]BF_4$.

Complex	**[1]BF$_4$**
Empirical formula	$C_{26}H_{18}BCuF_4N_6$
Formula weight	564.81
Crystal system	monoclinic
Space group	P 2 1/c
a (Å)	11.697(5)
b (Å)	11.601(5)
c (Å)	19.181(5)
a (°)	90°
β (°)	90.559(5)°
γ (°)	90°
V (Å^3)	2602.7(17)
Z	4
ρ_{calc} (g cm^{-3})	1.441
Radiation, *λ* (Å)	0.71069
μ (mm^{-1})	0.895
Temperature (K)	100(2)
Measd/independent reflns (R_{int})	11474/4567 (0.0274)
Parameters refined	343
GoF (on F^2)	1.052
R_1[a] ($I > 2\sigma(I)$)	0.0683
wR_2[b] ($I > 2\sigma(I)$)	0.0782
$(\Delta\rho)_{max}/(\Delta\rho)_{min}$ (e Å^{-3})	1.247 /-0.447

[a] $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma(|F_o|)$.

[b] $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°) for **[1]BF$_4$**.

Cu1–N1	2.009(4)	Cu1–N4	1.993(3)
Cu1–N2	2.006(4)	Cu1–N5	2.022(4)
N1–Cu1–N2	81.44(16)	N2–Cu1–N5	114.67(18)
N1–Cu1–N4	118.59(14)	N4–Cu1–N5	81.37(16)
N1–Cu1–N5	128.27(16)		
N2–Cu1–N4	139.86(15)		

Table 3. Crystal data and structure refinement for C26 H18 B Cu F4 N6 at 100 K.

Empirical formula	C26 H18 B Cu F4 N6
Formula weight	564.81
Temperature	100 K
Wavelength	0.71069 Å
Crystal system	N/A
Space group	N/A
Unit cell dimensions	a = 11.697(5) Å, α = 90.000(5)° b = 11.601(5) Å, β = 90.559(5)° c = 19.181(5) Å, γ = 90.000(5)°
Volume	2602.7(17) Å^3
Z	4
Density (calculated)	1.441 g/cm^3
Absorption coefficient	0.895 mm^{-1}
F(000)	1144
Crystal size	0.10 x 0.09 x 0.06 mm^3
θ range for data collection	3.249 to 24.999°
Index ranges	-9<=h<=13, -13<=k<=11, -22<=l<=22
Reflections collected	11474
Independent reflections	4567 [R_{int} = 0.0274]
Completeness to θ = 24.999°	99.8%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4567 / 0 / 343
Goodness-of-fit	1.052

Final R indices [I > 2σ(I)]	R_{obs} = 0.0683, wR_{obs} = 0.1845
R indices [all data]	R_{all} = 0.0782, wR_{all} = 0.1917
Extinction coefficient	.
Largest diff. peak and hole	1.247 and -0.447 e·Å^{-3}

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+(0.0931P)^2+5.7752P]$ where $P=(Fo^2+2Fc^2)/3$

Table 4. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for C26 H18 B Cu F4 N6 at 100 K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}^*
Cu(1)	7367(1)	2990(1)	9657(1)	1	47(1)
F(1)	6493(4)	5975(4)	8413(2)	1	108(2)
F(2)	7374(4)	7684(4)	8757(3)	1	115(2)
F(3)	6472(3)	7540(4)	7738(2)	1	89(2)
F(4)	5474(4)	7591(4)	8724(2)	1	99(2)
N(1)	6826(3)	4382(3)	10182(2)	1	43(1)
N(2)	8602(3)	4093(3)	9379(2)	1	55(2)
N(3)	9995(5)	5956(5)	8952(4)	1	118(3)
N(4)	7189(3)	1443(3)	10094(2)	1	35(1)
N(5)	6588(3)	2171(4)	8852(2)	1	51(1)
N(6)	6493(4)	-713(3)	10612(2)	1	62(2)
B(1)	6506(8)	7169(8)	8402(4)	1	97(3)
C(1)	5939(4)	4471(4)	10610(2)	1	44(1)
H(1)	5507.54	3812.9	10695.41	1	53
C(2)	5626(4)	5479(4)	10931(3)	1	50(2)
H(2)	5011.43	5497.03	11234.51	1	59
C(3)	6235(5)	6452(4)	10795(3)	1	69(2)
H(3)	6027.15	7153.71	10990.55	1	83
C(4)	7164(5)	6379(4)	10363(4)	1	81(2)
H(4)	7592.34	7034.87	10266.62	1	97
C(5)	7460(4)	5344(4)	10074(3)	1	57(2)
C(6)	8435(4)	5164(4)	9600(3)	1	64(2)
C(7)	9158(6)	6069(6)	9398(5)	1	105(3)
H(7)	9036.38	6793.22	9591.66	1	126
C(8)	10177(5)	4878(7)	8718(5)	1	97(2)
C(9)	9492(4)	3911(5)	8929(3)	1	66(2)
C(10)	9702(5)	2807(6)	8667(4)	1	78(2)
H(10)	9245.23	2189.67	8799.49	1	93
C(11)	10590(6)	2639(8)	8211(4)	1	97(2)
H(11)	10751.81	1907.67	8040.29	1	116
C(12)	11258(6)	3611(9)	8005(5)	1	118(3)
H(12)	11861.09	3494.69	7700.89	1	142
C(13)	11052(6)	4684(9)	8233(5)	1	124(3)
H(13)	11486.97	5298.27	8071.36	1	148
C(14)	6401(4)	2572(7)	8198(3)	1	77(2)

H(14)	6527.67	3349.31	8107.83	1	92
C(15)	6031(5)	1874(11)	7662(3)	1	114(4)
H(15)	5921.94	2169.34	7215.91	1	137
C(16)	5825(6)	736(11)	7800(3)	1	123(4)
H(16)	5562.46	256.38	7444.64	1	147
C(17)	6004(5)	289(7)	8463(3)	1	91(2)
H(17)	5871.24	-484.47	8561.47	1	109
C(18)	6393(4)	1054(5)	8978(2)	1	52(2)
C(19)	6641(4)	685(4)	9702(2)	1	43(1)
C(20)	6315(5)	-394(4)	9966(3)	1	58(2)
H(20)	5954.05	-908.99	9664.77	1	69
C(21)	7051(4)	57(4)	11037(3)	1	50(2)
C(22)	7420(4)	1140(4)	10776(2)	1	39(1)
C(23)	8039(4)	1896(4)	11207(3)	1	48(2)
H(23)	8282.3	2606.51	11039.89	1	58
C(24)	8278(5)	1569(6)	11880(3)	1	68(2)
H(24)	8700.51	2056.45	12168.7	1	82
C(25)	7894(6)	512(6)	12135(3)	1	79(2)
H(25)	8054.46	312.17	12595.57	1	95
C(26)	7298(6)	-223(5)	11730(3)	1	73(2)
H(26)	7050.07	-921.83	11912.21	1	87

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Anisotropic displacement parameters ($Å^2x10^3$) for C26 H18 B Cu F4 N6 at 100 K with estimated standard deviations in parentheses.

Label	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Cu(1)	45(1)	27(1)	68(1)	3(1)	10(1)	6(1)
F(1)	131(4)	105(3)	89(3)	-38(3)	55(2)	-19(2)
F(2)	106(3)	115(4)	125(4)	-46(3)	8(3)	-34(3)
F(3)	101(3)	100(3)	66(2)	-47(2)	42(2)	-25(2)
F(4)	126(3)	98(3)	75(2)	-69(3)	55(2)	-34(2)
N(1)	36(2)	25(2)	70(2)	1(2)	9(2)	10(2)
N(2)	38(2)	42(2)	86(3)	8(2)	19(2)	10(2)
N(3)	83(4)	74(4)	197(7)	-23(3)	82(5)	-15(4)
N(4)	32(2)	26(2)	46(2)	1(2)	9(2)	-3(2)
N(5)	34(2)	68(3)	49(2)	10(2)	8(2)	8(2)
N(6)	85(3)	26(2)	76(3)	-6(2)	47(2)	-6(2)

B(1)	118(7)	104(7)	69(5)	-83(6)	42(4)	-23(4)
C(1)	39(2)	30(2)	64(3)	1(2)	6(2)	12(2)
C(2)	43(2)	40(3)	65(3)	10(2)	13(2)	13(2)
C(3)	68(3)	27(2)	114(5)	5(2)	37(3)	0(3)
C(4)	80(4)	22(2)	143(6)	-8(3)	50(4)	4(3)
C(5)	47(3)	29(2)	95(4)	0(2)	28(3)	13(2)
C(6)	50(3)	34(3)	110(5)	-1(2)	34(3)	5(3)
C(7)	87(5)	55(4)	174(8)	-20(3)	76(5)	-10(4)
C(8)	53(3)	93(5)	145(7)	-8(3)	52(4)	5(5)
C(9)	41(3)	66(4)	91(4)	12(3)	17(3)	-2(3)
C(10)	61(4)	73(4)	99(5)	28(3)	20(3)	3(4)
C(11)	65(4)	111(6)	114(6)	42(4)	14(4)	-15(5)
C(12)	48(4)	143(8)	164(8)	8(5)	45(4)	-14(7)
C(13)	57(4)	132(8)	182(9)	-9(4)	67(5)	-32(7)
C(14)	39(3)	128(6)	63(4)	17(3)	14(3)	28(4)
C(15)	45(3)	251(13)	46(3)	-28(5)	3(3)	20(5)
C(16)	84(5)	236(12)	48(4)	-79(7)	18(3)	-29(5)
C(17)	76(4)	138(6)	58(3)	-58(4)	25(3)	-35(4)
C(18)	35(2)	72(4)	48(3)	-12(2)	15(2)	-16(2)
C(19)	40(2)	36(2)	53(3)	-7(2)	17(2)	-11(2)
C(20)	65(3)	39(3)	70(3)	-16(2)	36(3)	-21(2)
C(21)	61(3)	32(2)	58(3)	12(2)	27(2)	4(2)
C(22)	42(2)	30(2)	45(2)	9(2)	11(2)	2(2)
C(23)	46(3)	46(3)	53(3)	9(2)	1(2)	-8(2)
C(24)	67(3)	81(4)	56(3)	24(3)	-6(3)	-17(3)
C(25)	112(5)	79(4)	47(3)	53(4)	13(3)	9(3)
C(26)	107(5)	51(3)	61(3)	36(3)	41(3)	15(3)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table 6. Bond lengths [Å] for C26 H18 B Cu F4 N6 at 100 K with estimated standard deviations in parentheses.

Label	**Distances**
Cu(1)-N(4)	1.993(3)
Cu(1)-N(2)	2.006(4)
Cu(1)-N(1)	2.009(4)
Cu(1)-N(5)	2.022(4)
F(1)-B(1)	1.385(10)
F(2)-B(1)	1.356(9)
F(3)-B(1)	1.346(9)

F(4)-B(1)	1.446(11)
N(1)-C(1)	1.334(6)
N(1)-C(5)	1.356(6)
N(2)-C(6)	1.328(6)
N(2)-C(9)	1.376(6)
N(3)-C(7)	1.312(8)
N(3)-C(8)	1.347(9)
N(4)-C(19)	1.319(5)
N(4)-C(22)	1.380(5)
N(5)-C(18)	1.339(7)
N(5)-C(14)	1.353(7)
N(6)-C(20)	1.308(7)
N(6)-C(21)	1.371(7)
C(1)-C(2)	1.373(7)
C(2)-C(3)	1.362(7)
C(3)-C(4)	1.376(8)
C(4)-C(5)	1.369(7)
C(5)-C(6)	1.479(7)
C(6)-C(7)	1.406(8)
C(8)-C(13)	1.408(9)
C(8)-C(9)	1.438(9)
C(9)-C(10)	1.399(8)
C(10)-C(11)	1.378(9)
C(11)-C(12)	1.429(12)
C(12)-C(13)	1.342(12)
C(14)-C(15)	1.375(11)
C(15)-C(16)	1.368(14)
C(16)-C(17)	1.388(11)
C(17)-C(18)	1.400(8)
C(18)-C(19)	1.480(7)
C(19)-C(20)	1.403(7)
C(21)-C(26)	1.396(7)
C(21)-C(22)	1.421(6)
C(22)-C(23)	1.402(7)
C(23)-C(24)	1.371(7)
C(24)-C(25)	1.397(10)
C(25)-C(26)	1.344(10)

Table 7. Bond angles [°] for C26 H18 B Cu F4 N6 at 100 K with estimated standard deviations in parentheses.

Label	Angles
N(4)-Cu(1)-N(2)	139.86(15)
N(4)-Cu(1)-N(1)	118.59(14)
N(2)-Cu(1)-N(1)	81.44(16)
N(4)-Cu(1)-N(5)	81.37(16)
N(2)-Cu(1)-N(5)	114.67(18)
N(1)-Cu(1)-N(5)	128.27(16)
C(1)-N(1)-C(5)	117.4(4)
C(1)-N(1)-Cu(1)	128.4(3)
C(5)-N(1)-Cu(1)	114.2(3)
C(6)-N(2)-C(9)	117.4(4)
C(6)-N(2)-Cu(1)	113.8(3)
C(9)-N(2)-Cu(1)	128.3(4)
C(7)-N(3)-C(8)	115.6(6)
C(19)-N(4)-C(22)	117.4(4)
C(19)-N(4)-Cu(1)	114.4(3)
C(22)-N(4)-Cu(1)	127.5(3)
C(18)-N(5)-C(14)	118.3(5)
C(18)-N(5)-Cu(1)	113.1(3)
C(14)-N(5)-Cu(1)	127.8(5)
C(20)-N(6)-C(21)	116.7(4)
F(3)-B(1)-F(2)	110.4(5)
F(3)-B(1)-F(1)	109.5(6)
F(2)-B(1)-F(1)	116.2(9)
F(3)-B(1)-F(4)	106.2(8)
F(2)-B(1)-F(4)	105.1(6)
F(1)-B(1)-F(4)	108.8(5)
N(1)-C(1)-C(2)	123.6(4)
C(3)-C(2)-C(1)	118.6(4)
C(2)-C(3)-C(4)	118.9(5)
C(5)-C(4)-C(3)	120.1(5)
N(1)-C(5)-C(4)	121.3(4)
N(1)-C(5)-C(6)	113.8(4)
C(4)-C(5)-C(6)	124.9(4)
N(2)-C(6)-C(7)	121.3(5)
N(2)-C(6)-C(5)	116.4(4)

C(7)-C(6)-C(5)	122.3(5)
N(3)-C(7)-C(6)	124.0(6)
N(3)-C(8)-C(13)	119.1(7)
N(3)-C(8)-C(9)	122.7(5)
C(13)-C(8)-C(9)	118.2(7)
N(2)-C(9)-C(10)	120.2(5)
N(2)-C(9)-C(8)	118.9(5)
C(10)-C(9)-C(8)	120.9(6)
C(11)-C(10)-C(9)	119.5(7)
C(10)-C(11)-C(12)	118.8(8)
C(13)-C(12)-C(11)	122.8(7)
C(12)-C(13)-C(8)	119.8(8)
N(5)-C(14)-C(15)	122.4(8)
C(16)-C(15)-C(14)	118.6(7)
C(15)-C(16)-C(17)	120.8(7)
C(16)-C(17)-C(18)	117.0(8)
N(5)-C(18)-C(17)	122.7(6)
N(5)-C(18)-C(19)	114.7(4)
C(17)-C(18)-C(19)	122.6(6)
N(4)-C(19)-C(20)	121.5(4)
N(4)-C(19)-C(18)	115.5(4)
C(20)-C(19)-C(18)	123.0(4)
N(6)-C(20)-C(19)	123.6(5)
N(6)-C(21)-C(26)	120.6(5)
N(6)-C(21)-C(22)	120.7(4)
C(26)-C(21)-C(22)	118.7(5)
N(4)-C(22)-C(23)	119.7(4)
N(4)-C(22)-C(21)	120.1(4)
C(23)-C(22)-C(21)	120.2(4)
C(24)-C(23)-C(22)	118.8(5)
C(23)-C(24)-C(25)	120.6(6)
C(26)-C(25)-C(24)	121.4(5)
C(25)-C(26)-C(21)	120.3(6)

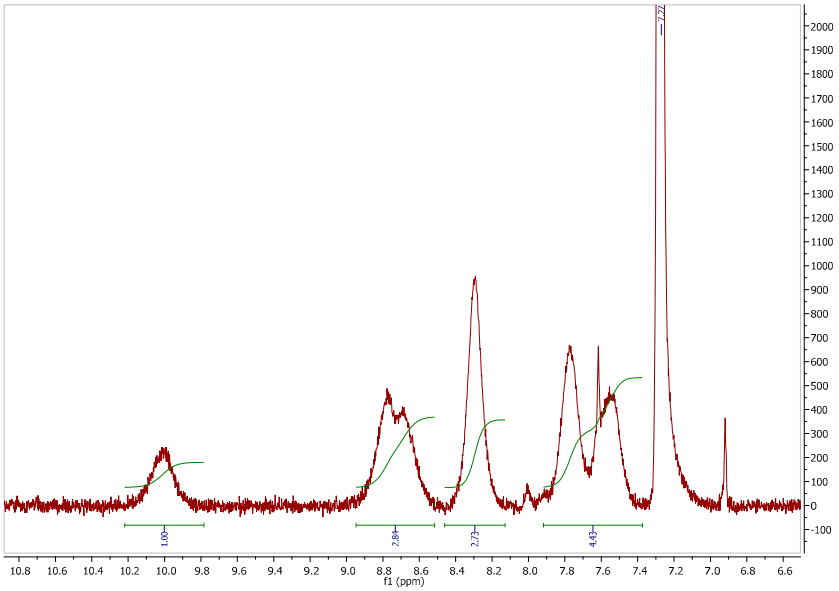

Figure S1. ^{1}H-NMR of **[1]BF$_4$** in $CDCl_3$.

Table 8. Electronic transitions of **[Cu(pq)$_2$]$^+$** calculated with the TDDFT method.

Orbitals	Character	λ	f
H-1 → L+1 H → L	Cu(I) d → pq π*, MLCT	562.9 nm	0.001
H-1 → L+1 H → L	Cu(I) d → pq π*, MLCT	509.0 nm	0.146
H-3 → L H-1 → L H → L+1	Cu(I) d → pq π* Cu(I) dx^2-y^2 & pq π → pq π*	452.2 nm	0.004
H-2 → L+1	Cu(I) d & N p → pq π*	417.0 nm	0.002
H-6 → L+1 H-5 → L+1 H-3 → L+1	pq π → pq π* Cu(I) dz^2 →pq π*	397.0 nm	0.05
H-6 → L H-4 → L+1 H-1 → L+3 H → L+2	Cu(I) dx^2-y^2 & pq π → pq π* pq π → pq π* Cu(I) d → pq π*	342.7 nm	0.308

Table 9. Performance of the photocatalytic systems with **[1]$^+$** as catalyst, different CdTe QDs as the photosensitizer and different e^- donors in DFM:H_2O 1:2 solvent mixture.

C_{cat} (μM)	QDs(20μM)	Donor	TON
1	CdTe QD's A*	TEOA C=0,5M	52.83
1	CdTe QD's B*	TEOA C=0,5M	49.12
1	CdTe QD's C*	TEOA C=0,5M	15.76
1	CdTe QD's D*	TEOA C=0,5M	132.53
1	CdTe QD's E*	TEOA C=0,5M	51.90

1	CdTe QD's F*	TEOA C=0,1M	34.29
1	CdTe QD's A*	AscOH C=0,1M	0
1	CdTe QD's B*	AscOH C=0,1M	0
1	CdTe QD's C*	AscOH C=0,1M	0
1	CdTe QD's D*	AscOH C=0,1M	0
1	CdTe QD's E*	AscOH C=0,1M	0
1	CdTe QD's F*	AscOH C=0,1M	0

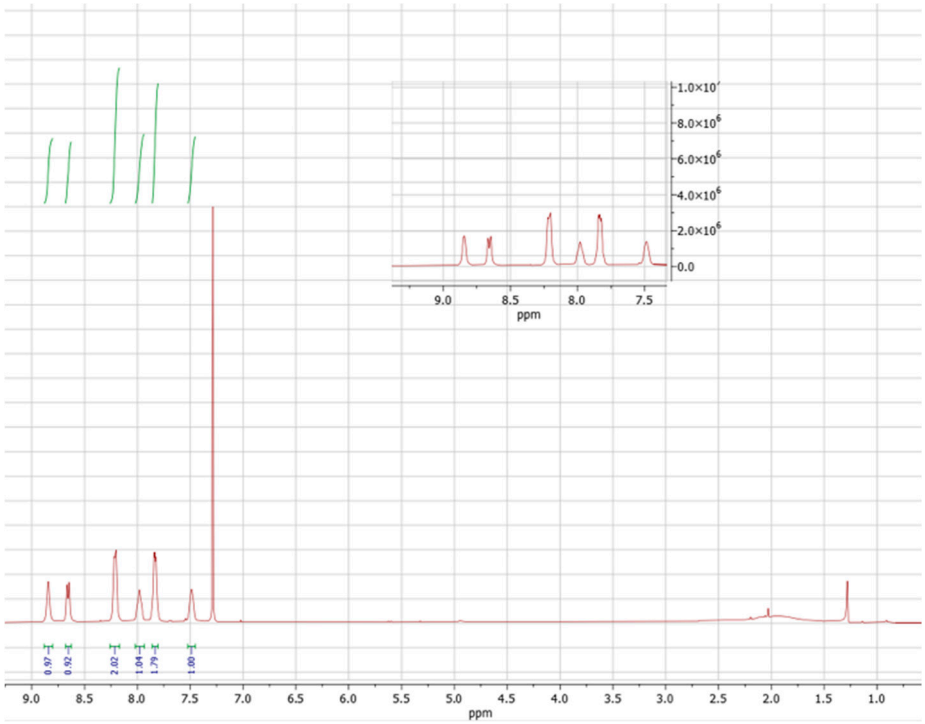

Figure S2. ^{1}H-NMR of **[Zn(pq)$_2$]$^{2+}$** in $CDCl_3$.

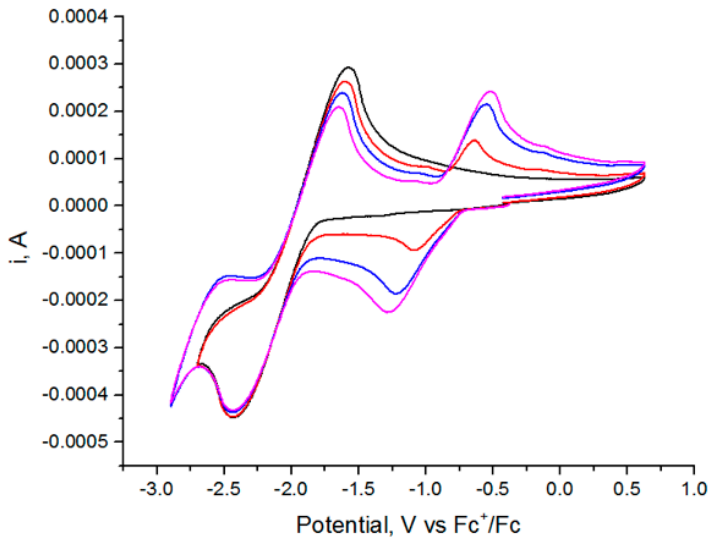

Figure S3. Cyclic voltammograms (CVs) of the pq ligand (5.0 mM) in the absence (black curve) and the presence (coloured curves) of 1mM (red), 2mM (blue) and 4mM (purple) of TFA recorded in a DMF solution of n-Bu_4NPF_6 (0.1 M) on a glassy carbon electrode at a scan rate of 0.1 V s^{-1}.

Tautomers of Catalytic Intermediates

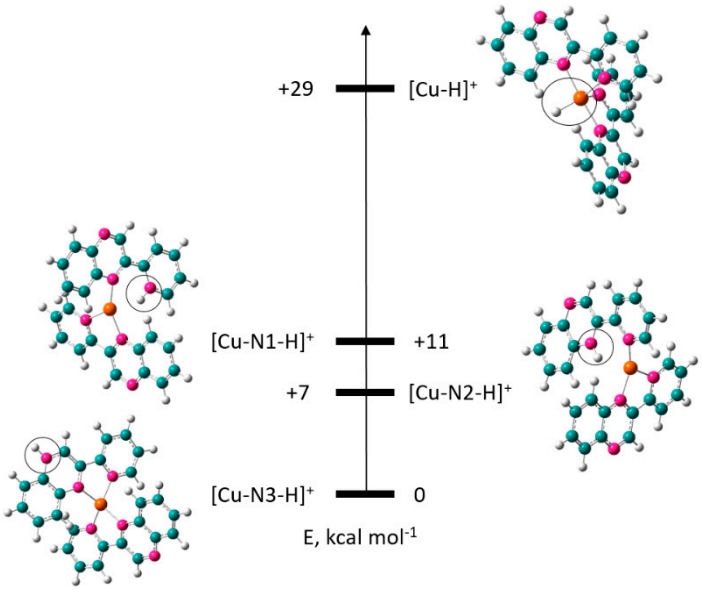

Figure S4. Relative free energies of the $1H^+$ protonated and $1e^-$ reduced species **[2]**$^+$ tautomers.

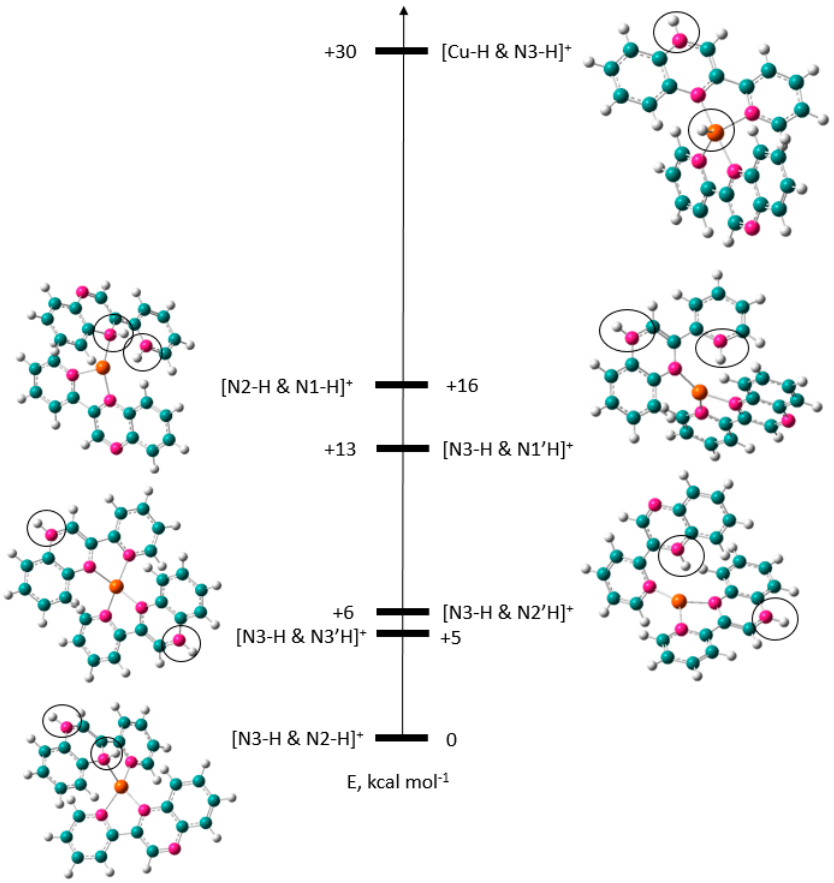

Figure S5. Relative free energies of the $2H^+$ protonated and $2e^-$ reduced species **[3]**$^+$ tautomers.

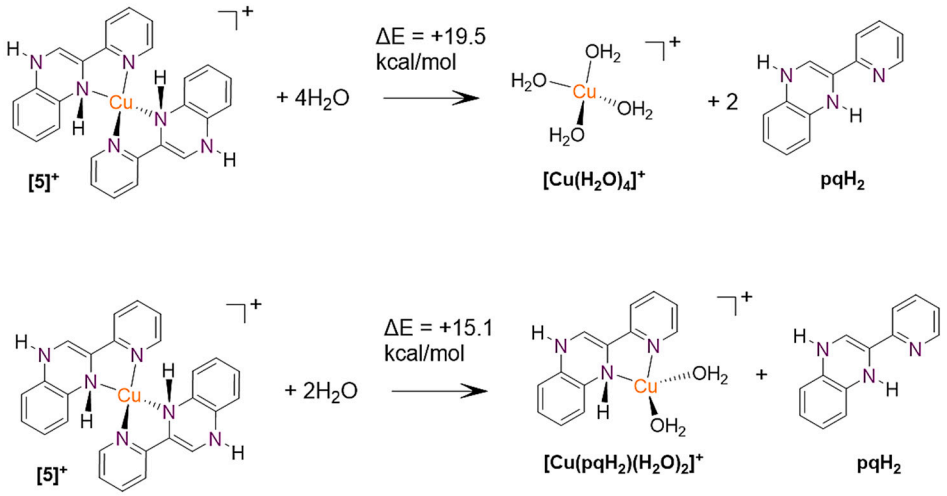

Figure S6. Possible decomposition pathways of the intermediate **[5]**$^+$ in water.

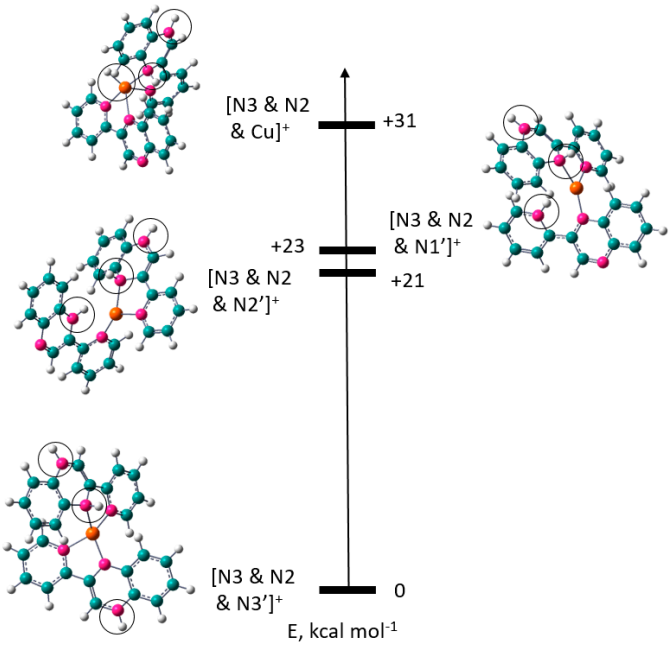

Figure S7. Relative free energies of the $3H^+$ protonated and $3e^-$ reduced species **[4]**$^+$ tautomers.

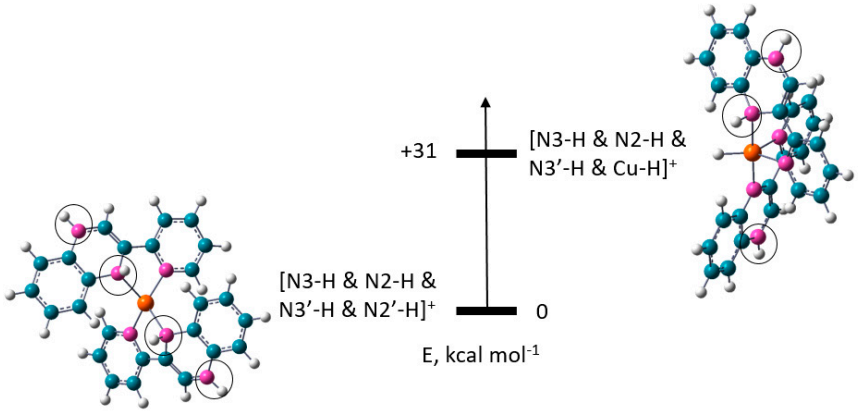

Figure S8. Relative free energies of the $4H^+$ protonated and $4e^-$ reduced species **[5]**$^+$ tautomers.

Electronic Structures of Catalytically Relevant Species:

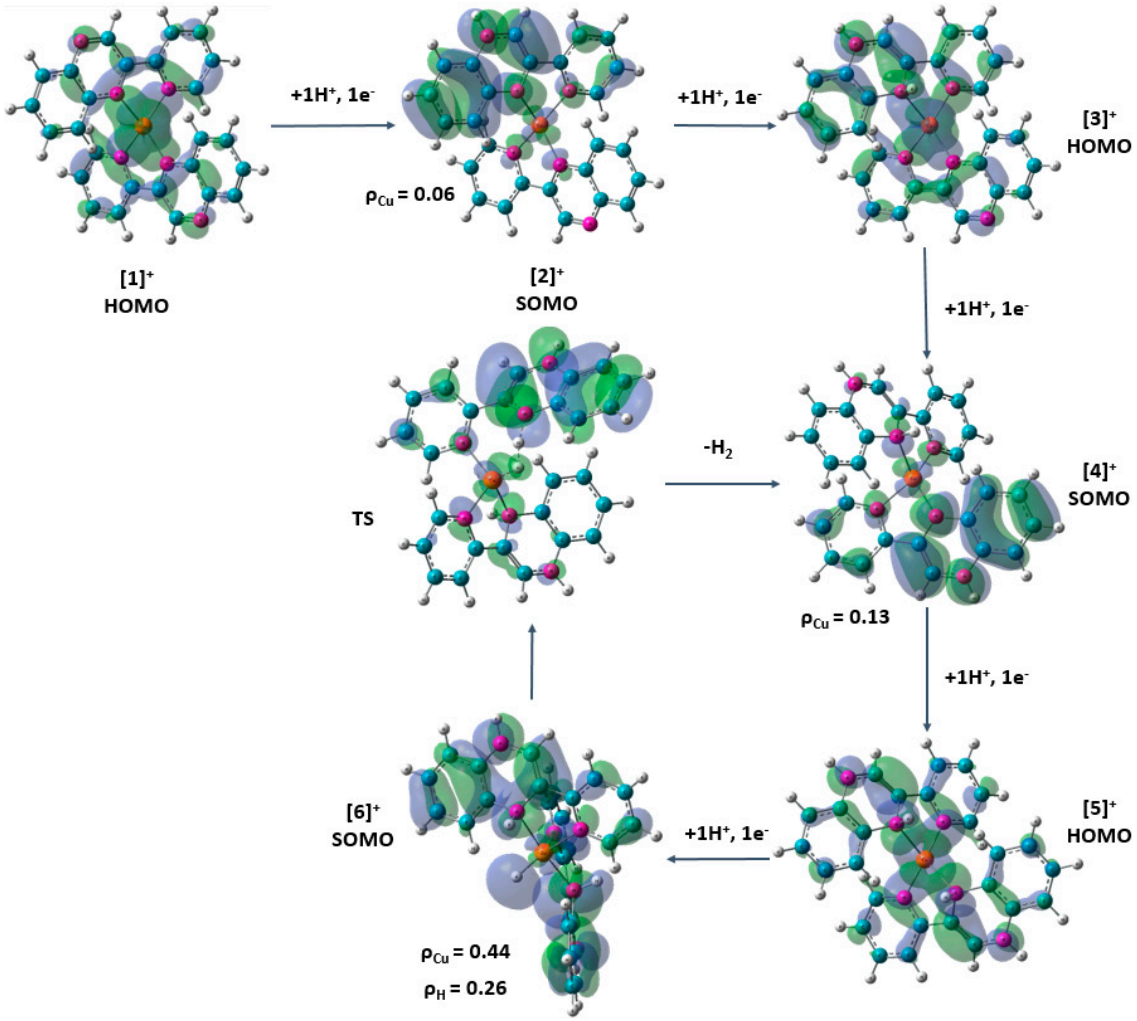

Figure S9. Higher occupied molecular orbital diagrams of the catalytic intermediates and spin densities on Cu (ϱ_{Cu}) of intermediates with unpaired electrons.

Table 10. Comparison of the experimental (crystal structure) and DFT calculated (B3LYP/6-31G**, gas phase) values of selected structural parameters of $[Cu(pq)_2]BF_4$ (**[1]BF_4**).

Bond lengths	Crystal	Calculated	Bond Angles	Crystal	Calculated
Cu-N1	2.009	2.004	N1-Cu-N1′	128.3	128.2
Cu-N1′	2.022	2.004	N2-Cu-N2′	139.9	135.7
Cu-N2	2.006	1.983	N1-Cu-N2	81.4	82.9
Cu-N2′	1.993	1.983	N1-Cu-N2′	118.6	117.0
C1-C2	1.479	1.476	N2′-Cu-N1′	81.4	82.9
C1′-C2′	1.480	1.476	N2-Cu-N1′	114.7	116.9

Table 11. The free energy of H_2 self-elimination from AH_2 was calculated from the following equations.

Reactant	Product	Free Energy

$\mathbf{AH_2}$	→	$\mathbf{AH^-} + H^+$	ln(10)RTpKa
$\mathbf{AH_2^-}$	→	$\mathbf{AH} + e^-$	FE^o
$\mathbf{AH}$	→	$\mathbf{A^-} + H^+$	ln(10)RTpKa
$\mathbf{A^-}$	→	$\mathbf{A} + e^-$	FE^o
$2H^+ + 2e^-$	→	H_2	$-2FE^o(H^+/H_2)$
$\mathbf{AH_2}$	→	$\mathbf{A} + H_2$	ΔG^o

Molecular Geometries and Gibbs Free Energies

[1]+

1 1

C	1.61165000	-2.24954000	-1.04149700
C	2.03265000	-3.51241600	-1.47267600
C	1.18009600	-4.28382000	-2.25655100
C	-0.07655600	-3.77823500	-2.58939500
C	-0.43059600	-2.51811100	-2.11960800
N	0.38480800	-1.76262700	-1.36462900
H	1.49163900	-5.26498900	-2.59898300
H	3.00607500	-3.89614100	-1.19341400
H	-0.77085200	-4.34374200	-3.20040800
H	-1.39922700	-2.08790400	-2.35308800
Cu	-0.00008200	-0.00087600	-0.49012600
C	2.43244600	-1.35025900	-0.20645500
C	3.80059300	-1.59837700	0.09637800
N	1.81887200	-0.25422700	0.25774300
N	4.52906100	-0.79509000	0.83588100
H	4.29900100	-2.47872300	-0.29925500
C	2.54772200	0.60323000	1.03989300
C	3.92040400	0.31999700	1.32840900
C	4.65985700	1.21444900	2.13996400
C	1.94972000	1.76879300	1.57367100
H	0.90579400	1.96835400	1.35630600
H	5.69820600	0.97523800	2.34134200
C	2.69395500	2.61918400	2.36173100
C	4.05505900	2.34344600	2.64588500
H	2.23411700	3.51115000	2.77503800
H	4.61912100	3.02895600	3.26977900
N	-1.81930700	0.25432600	0.25671100
C	-2.43187600	1.35056500	-0.20827100
C	-2.54909000	-0.60222100	1.03897200
C	-3.79997200	1.59983700	0.09389500
C	-3.92166600	-0.31783000	1.32684800
N	-4.52931100	0.79746400	0.83351700
H	-4.29759100	2.48028800	-0.30250100
C	-1.61015100	2.24875800	-1.04358000
C	-2.03001100	3.51174100	-1.47557900
N	-0.38366900	1.76064200	-1.36611100
C	-1.17670400	4.28186300	-2.25988600
H	-3.00309900	3.89651500	-1.19657900
C	0.43248900	2.51489600	-2.12150200
C	0.07954700	3.77495500	-2.59227500

H	-1.48734600	5.26307500	-2.60301700
H	1.40084000	2.08375800	-2.35444000
H	0.77435000	4.33941700	-3.20367700
C	-4.66207800	-1.21133300	2.13856100
C	-1.95215800	-1.76799600	1.57349200
H	-5.70032200	-0.97126200	2.33945500
H	-0.90830400	-1.96844000	1.35657700
C	-4.05830800	-2.34055300	2.64522400
C	-2.69731700	-2.61746000	2.36167800
H	-4.62311500	-3.02534700	3.26923000
H	-2.23830800	-3.50959100	2.77555200

E = -2970.373828

[2]$^{+}$ (first proton addition to N3, [Cu-N3-H]$^{+}$)

1 2

C	-1.43278600	2.38857000	-0.98804100
C	-1.73306100	3.69689300	-1.38450700
C	-0.79702500	4.41575100	-2.12100100
C	0.42090900	3.81394300	-2.44014200
C	0.65376900	2.51436000	-2.00436100
N	-0.24444200	1.80808600	-1.29763000
H	-1.01328700	5.43098500	-2.43661300
H	-2.67593800	4.15444000	-1.11105800
H	1.17665500	4.33678500	-3.01525400
H	1.58829400	2.00885600	-2.22550900
Cu	-0.00615600	0.00926800	-0.42818200
C	-2.34521600	1.53657400	-0.20295400
C	-3.70978100	1.86269400	0.03336300
N	-1.81938500	0.40286000	0.27937700
N	-4.52121900	1.09878100	0.72688200
H	-4.13448200	2.77266500	-0.38138400
C	-2.63599400	-0.41404100	1.01814900
C	-4.00244700	-0.05293900	1.23982800
C	-4.83166600	-0.90707500	2.00659700
C	-2.13235600	-1.61286800	1.57504000
H	-1.09109700	-1.86864600	1.41082500
H	-5.86355000	-0.60951100	2.15722300
C	-2.96291700	-2.42242600	2.31896400
C	-4.31876300	-2.07102800	2.53486000
H	-2.57548300	-3.33988200	2.75040500
H	-4.95219800	-2.72524300	3.12497000
N	1.78391000	-0.37969300	0.24888100
C	2.29811500	-1.56079600	-0.24224500

C	2.63971800	0.43615300	0.97559500
C	3.61006500	-1.92511000	-0.04683500
C	4.00021600	0.09045300	1.20044200
N	4.44809600	-1.11360300	0.65941900
H	4.04178000	-2.83433500	-0.43986000
C	1.35488600	-2.39818000	-1.00502600
C	1.62111000	-3.70933300	-1.42467000
N	0.16391300	-1.80511500	-1.27749700
C	0.65972400	-4.40636900	-2.14424000
H	2.56170900	-4.18814600	-1.17957700
C	-0.76276300	-2.49299900	-1.96984200
C	-0.56100900	-3.78744200	-2.42693600
H	0.85507000	-5.42129600	-2.47458400
H	-1.69697300	-1.97344300	-2.15797900
H	-1.33875100	-4.29561800	-2.98527300
C	4.84659200	0.92334000	1.93329800
C	2.17303500	1.64292100	1.52473900
H	5.88252800	0.63514600	2.08971100
H	1.13251900	1.90682800	1.36909300
C	4.35537400	2.11552600	2.45971900
C	3.01694400	2.47141100	2.25488400
H	5.01279600	2.76166900	3.03119100
H	2.63305900	3.39642400	2.67209700
H	5.41171300	-1.38357200	0.79476500

E = -2970.965599

[2]$^{+}$ (first proton addition to N2, [Cu-N2-H]$^{+}$)

1 2

C	-2.21051000	-1.26503400	-1.72294400
C	-2.87846100	-1.48898800	-2.92897900
C	-2.33463300	-2.38484900	-3.84843100
C	-1.13873200	-3.02987300	-3.54232600
C	-0.52741300	-2.74835000	-2.32227600
N	-1.04396100	-1.89133700	-1.43035900
H	-2.83895400	-2.57095800	-4.79083800
H	-3.79950400	-0.96872200	-3.16086800
H	-0.68377400	-3.73583300	-4.22759900
H	0.40643700	-3.22521100	-2.04152100
Cu	-0.21169100	-1.14311600	0.27098700
C	-2.69670300	-0.33920800	-0.67320300
C	-3.99011900	0.25131700	-0.69425500
N	-1.84873300	-0.08073300	0.32916000
N	-4.41790200	1.07022700	0.23952600

H	-4.68368100	0.02660000	-1.49902900
C	-2.26819400	0.75423400	1.33144800
C	-3.57296300	1.34281600	1.27007300
C	-3.99085900	2.21711700	2.30311300
C	-1.42182100	1.04592400	2.42615700
H	-0.44236000	0.58009300	2.47177000
H	-4.98306400	2.64859600	2.23151300
C	-1.85786800	1.89800200	3.41688800
C	-3.14545000	2.48908400	3.35539800
H	-1.20975600	2.12016900	4.25839400
H	-3.46293700	3.15733300	4.14892300
N	1.75175500	0.78637800	-0.02033900
C	2.83915600	0.00011300	0.31174500
C	1.88499700	1.96845900	-0.73432700
C	4.09661800	0.45184100	-0.15807900
C	3.19415000	2.33101400	-1.15027400
N	4.29596600	1.54801700	-0.85624600
H	4.97614100	-0.15420600	0.04064000
C	2.63626900	-1.21779800	1.05971700
C	3.71213300	-1.88109400	1.69723200
N	1.36202200	-1.72130900	1.16840600
C	3.49439300	-3.03490600	2.42108800
H	4.70755200	-1.45996600	1.64031800
C	1.17071900	-2.85086800	1.89887900
C	2.18641000	-3.53685400	2.53103100
H	4.32214700	-3.53399500	2.91367900
H	0.14624000	-3.20241400	1.96994300
H	1.96618100	-4.43212900	3.09997300
C	3.36098500	3.52067000	-1.88007300
C	0.78583900	2.77932600	-1.03714300
H	4.36637500	3.78271700	-2.19099500
H	-0.20783800	2.49467900	-0.70222700
C	2.26911200	4.32378700	-2.18097700
C	0.98370900	3.95281600	-1.75786500
H	2.40889500	5.24146500	-2.74227200
H	0.13357800	4.58572800	-1.99118900
H	0.83877300	0.52552100	0.35204900

E = -2970.928440

[2]$^{+}$ (first proton addition to N1, [Cu-N1-H]$^{+}$)

1 2

C	-1.65573800	2.22059500	-1.21631100
C	-2.16455300	3.21042100	-2.09461800

C	-1.32161900	4.06537600	-2.76788900
C	0.08854700	3.97143500	-2.59828000
C	0.57530300	3.01136200	-1.75899300
N	-0.27795600	2.17618500	-1.09897200
H	-1.73606900	4.81175900	-3.43643200
H	-3.23256200	3.28881000	-2.24607200
H	0.76670200	4.63585500	-3.11840100
H	1.62991500	2.85810100	-1.56441900
Cu	-0.06970600	-0.44174800	0.09446600
C	-2.43302900	1.28836000	-0.45271300
C	-3.86133100	1.40885000	-0.39842900
N	-1.81746100	0.29227500	0.26048700
N	-4.64603200	0.64551900	0.30844000
H	-4.34864600	2.19237700	-0.97180200
C	-2.62607300	-0.48815100	1.07129000
C	-4.03926300	-0.32231600	1.07994300
C	-4.83162700	-1.15566400	1.89180700
C	-2.04715600	-1.47079600	1.90116500
H	-0.96375100	-1.56465200	1.94503700
H	-5.90543500	-1.00383400	1.87146600
C	-2.84512300	-2.27596700	2.69569700
C	-4.24467400	-2.12531100	2.68794100
H	-2.38661400	-3.02181100	3.33712600
H	-4.85988000	-2.76133600	3.31545200
N	1.86270600	-0.29861700	0.29893600
C	2.55301500	-1.23512900	-0.36798300
C	2.55474800	0.53894400	1.13678800
C	3.96454000	-1.32716800	-0.22541400
C	3.97746900	0.42014900	1.24834400
N	4.66168200	-0.52681500	0.54847900
H	4.51935400	-2.09430200	-0.75762400
C	1.76233400	-2.15091100	-1.21798600
C	2.32584800	-3.03718700	-2.14072800
N	0.41981800	-2.07470900	-1.03598600
C	1.48747100	-3.87209200	-2.87636600
H	3.39718000	-3.07215600	-2.29603400
C	-0.37850900	-2.88105300	-1.75060500
C	0.10966900	-3.79898800	-2.67726200
H	1.90666100	-4.56756300	-3.59591400
H	-1.44356500	-2.78619100	-1.56310000
H	-0.57616200	-4.43685200	-3.22293000
C	4.68265000	1.29784000	2.10673000
C	1.87572200	1.52471000	1.88981000

H	5.75909100	1.18487300	2.17294400
H	0.79474500	1.59508200	1.81416700
C	3.99844800	2.25096300	2.82905400
C	2.58992700	2.36101400	2.72133900
H	4.53671600	2.92186900	3.49028400
H	2.06758200	3.11198700	3.30517000
H	0.09492500	1.44611000	-0.48610300

E = -2970.926059

[2]$^{+}$ (first proton addition to Cu, [Cu-H]$^{+}$)

1 2

C	-1.25099400	2.18609600	-1.14649700
C	-1.47054300	3.27315800	-1.99992700
C	-0.38710700	3.84599100	-2.66151400
C	0.88668900	3.31995000	-2.45779000
C	1.02219000	2.23236100	-1.59834200
N	-0.01251100	1.67731400	-0.95544900
H	-0.53912200	4.68983000	-3.32640900
H	-2.46662500	3.66753400	-2.15613200
H	1.75753400	3.73636300	-2.95116100
H	1.99472600	1.78967400	-1.40818000
Cu	-0.00000700	0.00000300	0.37048100
C	-2.32980000	1.51365400	-0.38805000
C	-3.67406100	1.98559400	-0.37323500
N	-1.99356500	0.42021100	0.29732200
N	-4.63880300	1.37666000	0.27488600
H	-3.94627200	2.88847100	-0.91142600
C	-2.96679900	-0.23278300	1.00409300
C	-4.31378700	0.25415300	0.97168700
C	-5.32485500	-0.44085900	1.67968600
C	-2.66160900	-1.39151800	1.75744800
H	-1.63164400	-1.72247300	1.81028800
H	-6.33467100	-0.04814000	1.63700900
C	-3.66731300	-2.04337900	2.43564800
C	-5.00463900	-1.57205200	2.39523100
H	-3.43323800	-2.92742200	3.02009600
H	-5.77488400	-2.10562800	2.94235200
N	1.99361000	-0.42031200	0.29739500
C	2.32976700	-1.51356600	-0.38835700
C	2.96694400	0.23248100	1.00417900
C	3.67406600	-1.98539500	-0.37401400
C	4.31395300	-0.25439100	0.97139000
N	4.63890400	-1.37661800	0.27412400

H	3.94625800	-2.88803800	-0.91260500
C	1.25088200	-2.18584600	-1.14680900
C	1.47024000	-3.27284700	-2.00037100
N	0.01246800	-1.67697000	-0.95559400
C	0.38669100	-3.84547500	-2.66194300
H	2.46625700	-3.66733200	-2.15670800
C	-1.02234500	-2.23179700	-1.59849700
C	-0.88702800	-3.31929700	-2.45808400
H	0.53856400	-4.68925300	-3.32694900
H	-1.99480300	-1.78899700	-1.40820900
H	-1.75795500	-3.73555300	-2.95144000
C	5.32510000	0.44044300	1.67945300
C	2.66181300	1.39095500	1.75797000
H	6.33493200	0.04779800	1.63647300
H	1.63183000	1.72181700	1.81107100
C	5.00493800	1.57137200	2.39543300
C	3.66759200	2.04262600	2.43623200
H	5.77524800	2.10479900	2.94260900
H	3.43357500	2.92645500	3.02102700
H	-0.00012700	0.00025100	1.90542800

E = -2970.914365

[3]$^{+}$ (second proton addition to N2, [N3-H & N2-H]$^{+}$)

1 1

C	1.02123100	-2.36241000	-1.11047800
C	1.05672200	-3.68166500	-1.57768200
C	-0.05194200	-4.20067100	-2.23784700
C	-1.17511800	-3.39099900	-2.41109600
C	-1.14192600	-2.09373800	-1.91272700
N	-0.07500300	-1.57616100	-1.27870100
H	-0.04071900	-5.22091600	-2.60668600
H	1.93015400	-4.30122100	-1.41530900
H	-2.05945000	-3.75248100	-2.92354700
H	-1.99474800	-1.43273700	-2.02675800
Cu	0.08074500	0.17070900	-0.29272600
C	2.13924500	-1.71688700	-0.39912200
C	3.44882500	-2.27057500	-0.34590700
N	1.86345200	-0.54612800	0.19425900
N	4.44940000	-1.69589000	0.27929400
H	3.66592800	-3.20789700	-0.85058800
C	2.89129300	0.08621000	0.84917000
C	4.19247600	-0.50541000	0.89312400
C	5.23543400	0.15700200	1.58470200

C	2.67241700	1.32758100	1.49050600
H	1.68515300	1.77471100	1.44023200
H	6.21099400	-0.31636200	1.60176800
C	3.70670300	1.95090500	2.15472600
C	4.99453500	1.36311900	2.20497500
H	3.53571800	2.90349300	2.64602000
H	5.79331500	1.87101700	2.73543300
N	-1.62146400	0.70628700	0.80990300
C	-2.19114100	1.83318400	0.06530700
C	-2.59844900	-0.31881600	1.17040900
C	-3.52209600	2.07014300	0.11363000
C	-3.96726300	-0.00862300	1.22766800
N	-4.38458500	1.26445200	0.81229900
H	-3.97482900	2.88480300	-0.43774800
C	-1.23358600	2.63054600	-0.70032000
C	-1.47860000	3.94553900	-1.12812000
N	-0.05103300	2.01757800	-0.97405600
C	-0.51524800	4.61430300	-1.87041700
H	-2.40467700	4.44191100	-0.86199100
C	0.88133600	2.68444000	-1.68075800
C	0.69368000	3.97360300	-2.15723600
H	-0.69587000	5.62976600	-2.20793200
H	1.80844500	2.15003800	-1.86120700
H	1.47599400	4.46426200	-2.72443300
C	-4.88254300	-0.97131100	1.66051900
C	-2.16518400	-1.58734600	1.54141800
H	-5.94026800	-0.72608000	1.70050100
H	-1.10498100	-1.81447000	1.49541800
C	-4.43486700	-2.23281600	2.04955500
C	-3.07708500	-2.54506600	1.99121900
H	-5.15175800	-2.97014700	2.39526300
H	-2.72525900	-3.52471500	2.29567000
H	-1.23734900	1.07672600	1.68323900
H	-5.37586800	1.42731200	0.71942400

E = -2971.555031

[3]$^{+}$ (second proton addition to N3′, [N3-H & N3′-H]$^{+}$)

1 3

C	1.20456900	-2.49551400	-0.95369400
C	1.37722400	-3.82447600	-1.36818000
C	0.34950900	-4.46863100	-2.04298500
C	-0.84380000	-3.78099800	-2.28543300
C	-0.95182000	-2.47363800	-1.83487100

N	0.04123900	-1.83657600	-1.18809200
H	0.47136400	-5.49636800	-2.36913900
H	2.29648500	-4.35586400	-1.15179300
H	-1.67091900	-4.24808100	-2.80755000
H	-1.86045600	-1.90015200	-1.98768000
Cu	-0.00003900	0.00004100	-0.34784400
C	2.21928000	-1.70542500	-0.23782200
C	3.51841400	-2.13174200	-0.09947000
N	1.78344700	-0.49736600	0.26859800
N	4.42738700	-1.35739600	0.56077100
H	3.88654300	-3.06299100	-0.50564700
C	2.70999800	0.27801200	0.95399100
C	4.06178200	-0.13107100	1.11562500
C	4.97988900	0.66253700	1.80375800
C	2.32603700	1.50309300	1.52517500
H	1.29164300	1.81292100	1.42383500
H	6.00756000	0.32610100	1.91124800
C	3.24238400	2.29319100	2.21053400
C	4.57119200	1.87752300	2.34966000
H	2.92084900	3.23386700	2.64523200
H	5.28511000	2.49255800	2.88671500
N	-1.78340300	0.49731100	0.26906100
C	-2.21932600	1.70549400	-0.23698700
C	-2.70982400	-0.27821700	0.95446100
C	-3.51842300	2.13180100	-0.09826000
C	-4.06156800	0.13085000	1.11647300
N	-4.42726900	1.35731400	0.56199000
H	-3.88662300	3.06315200	-0.50413800
C	-1.20474700	2.49572500	-0.95288900
C	-1.37744000	3.82479500	-1.36701400
N	-0.04150200	1.83679100	-1.18771100
C	-0.34984600	4.46907000	-2.04188900
H	-2.29662900	4.35616900	-1.15029400
C	0.95144100	2.47396700	-1.83455300
C	0.84337900	3.78144300	-2.28476900
H	-0.47173000	5.49689000	-2.36776800
H	1.86001700	1.90047800	-1.98770500
H	1.67040300	4.24861800	-2.80695600
C	-4.97954300	-0.66290400	1.80461400
C	-2.32576300	-1.50343700	1.52527800
H	-6.00718500	-0.32647600	1.91240100
H	-1.29139500	-1.81325800	1.42364900
C	-4.57075100	-1.87802500	2.35014400

C	-3.24198000	-2.29368200	2.21064100
H	-5.28456700	-2.49317400	2.88720500
H	-2.92036900	-3.23446600	2.64505000
H	-5.38178400	1.67250500	0.65537600
H	5.38192700	-1.67259300	0.65388100

E = -2971.557356

[3]$^{+}$ (second proton addition to N2′, [N3-H & N2′-H]$^{+}$)

1 1

C	-2.76097100	-1.07213100	-1.20960000
C	-3.69700100	-1.33816100	-2.22371400
C	-3.59546800	-2.50742300	-2.96007800
C	-2.54865300	-3.39968200	-2.69120400
C	-1.64838700	-3.06897700	-1.69261200
N	-1.74169200	-1.94127800	-0.95950600
H	-4.31511700	-2.72225300	-3.74327400
H	-4.48503200	-0.62810900	-2.44512300
H	-2.43526500	-4.32440900	-3.24482900
H	-0.81591200	-3.72269000	-1.45042100
Cu	-0.43959300	-1.15685700	0.34663200
C	-2.76945000	0.11883200	-0.35813900
C	-3.84034000	0.97120500	-0.30167200
N	-1.62291900	0.32296400	0.41035000
N	-3.81533900	2.05775700	0.52232300
H	-4.74172700	0.82933300	-0.88103700
C	-1.64754700	1.37618600	1.32017000
C	-2.73812600	2.28812000	1.38420400
C	-2.72945700	3.36285900	2.26979700
C	-0.57613900	1.58825800	2.20133700
H	0.24138600	0.87452600	2.19170100
H	-3.57673400	4.04296000	2.29553200
C	-0.56751500	2.66453700	3.08669600
C	-1.63951300	3.55799400	3.12078500
H	0.27451300	2.79968400	3.75751300
H	-1.63802000	4.39477600	3.81048100
N	1.82492200	0.41783500	-0.32266600
C	2.79411600	-0.47288000	0.03213900
C	2.07714800	1.53298700	-1.09518300
C	4.10286300	-0.18879800	-0.45007800
C	3.42156600	1.73886700	-1.51443500
N	4.41776200	0.85481600	-1.18044600
H	4.91048500	-0.87871300	-0.22875600
C	2.45756100	-1.63332200	0.83444600

C	3.47452800	-2.41334700	1.43233000
N	1.13325400	-1.95614300	1.01931300
C	3.15646900	-3.51868100	2.19394100
H	4.51115900	-2.12613400	1.31563300
C	0.84741700	-3.05104100	1.77815100
C	1.80282100	-3.85002500	2.36823400
H	3.93902800	-4.10897600	2.65783700
H	-0.20647800	-3.27038800	1.91233200
H	1.50001600	-4.70494000	2.96137200
C	3.72096000	2.87366100	-2.29483200
C	1.06188300	2.43141000	-1.45356700
H	4.74946500	3.01560500	-2.60739900
H	0.04237000	2.25324800	-1.12759200
C	2.71832700	3.76317200	-2.63971800
C	1.39172600	3.53923900	-2.21936800
H	2.95057000	4.63641100	-3.23982100
H	0.61473200	4.24250900	-2.50077900
H	0.86530100	0.23482400	0.00330800
H	-4.62134000	2.66277000	0.57724900

E = -2971.514290

[3]$^{+}$ (second proton addition to N1, [N3-H & N1-H]$^{+}$)

1 3

C	1.79657700	-2.14859700	-1.23049900
C	2.36773500	-3.10656400	-2.10878400
C	1.58088400	-3.98915400	-2.81074700
C	0.16200100	-3.96072200	-2.67299000
C	-0.38512000	-3.03510700	-1.83403800
N	0.41287400	-2.16850700	-1.14499600
H	2.04367200	-4.70788700	-3.47790100
H	3.44153200	-3.13544500	-2.23582600
H	-0.47320700	-4.64775300	-3.21735700
H	-1.44972300	-2.93158200	-1.66166200
Cu	0.05640200	0.40413300	0.05811800
C	2.51296700	-1.19580600	-0.43950800
C	3.94345500	-1.26126900	-0.34212400
N	1.83766300	-0.23504800	0.27185600
N	4.67547900	-0.48843800	0.40836000
H	4.47831900	-2.01097000	-0.91876100
C	2.58957300	0.55528100	1.12605700
C	4.00629200	0.43765200	1.18272200
C	4.73979400	1.27592600	2.04232100
C	1.94976900	1.50292100	1.95181300

H	0.86347900	1.56548600	1.94938000
H	5.81822300	1.15981600	2.05748500
C	2.69087200	2.31362200	2.79506400
C	4.09308100	2.20710300	2.83907600
H	2.18419900	3.03186100	3.43199200
H	4.66407300	2.84790500	3.50258900
N	-1.85326500	0.23947900	0.27351400
C	-2.57992100	1.18187900	-0.41619300
C	-2.54399500	-0.60877200	1.12827800
C	-3.94865600	1.27551500	-0.29729400
C	-3.95798100	-0.54779400	1.26445500
N	-4.62540200	0.41659300	0.51572500
H	-4.54184300	2.01861500	-0.81015100
C	-1.79765900	2.10473100	-1.26970600
C	-2.36428400	3.02041100	-2.16436800
N	-0.45500300	2.00466300	-1.12578700
C	-1.53089400	3.85638100	-2.90016800
H	-3.43784300	3.07898100	-2.29919500
C	0.34180600	2.81445000	-1.84122600
C	-0.14855200	3.75874600	-2.73596700
H	-1.95567900	4.57215900	-3.59634300
H	1.40868200	2.69250700	-1.68167200
H	0.53451000	4.39383200	-3.28813800
C	-4.64013200	-1.41593900	2.11984600
C	-1.85191800	-1.56842300	1.88873400
H	-5.72101900	-1.34880300	2.20620900
H	-0.77066600	-1.61122100	1.80122300
C	-3.92704900	-2.35623300	2.85651900
C	-2.53177800	-2.42847800	2.74047700
H	-4.45539400	-3.02977900	3.52232800
H	-1.97765300	-3.15843300	3.32079400
H	-5.62792000	0.50291100	0.61016000
H	-0.00903400	-1.47380900	-0.52179300

E = -2971.520599

[3]$^{+}$ (second proton addition to Cu, [N3-H & Cu-H]$^{+}$)

1 3

C	-1.21329400	-2.20879800	1.12940500
C	-1.39181300	-3.32609400	1.95724700
C	-0.28855000	-3.89785700	2.57909100
C	0.97470600	-3.34421200	2.36647100
C	1.07192100	-2.23511900	1.53500400
N	0.01360600	-1.67857200	0.92696000

H	-0.41320900	-4.76364900	3.22126600
H	-2.37563300	-3.74903300	2.12038700
H	1.86165100	-3.75797900	2.83233900
H	2.03175500	-1.76981800	1.33605800
Cu	0.00696800	0.00546800	-0.38547700
C	-2.31252800	-1.52518400	0.41578200
C	-3.61860900	-1.96116700	0.49476400
N	-1.95942500	-0.43600500	-0.33470800
N	-4.60074700	-1.29487000	-0.17412300
H	-3.92828100	-2.82665500	1.06176600
C	-2.95604800	0.23412000	-1.02485000
C	-4.31663800	-0.17702000	-0.95304500
C	-5.31959200	0.51048000	-1.63884300
C	-2.64972700	1.35476400	-1.81939900
H	-1.61009700	1.64540100	-1.90501700
H	-6.35036900	0.17485800	-1.56589100
C	-3.65024600	2.03522900	-2.50000600
C	-4.98557900	1.61826400	-2.41153300
H	-3.39227800	2.89364900	-3.11119600
H	-5.76235400	2.15319000	-2.94715600
N	2.00913900	0.42291100	-0.27566100
C	2.33929300	1.51298300	0.41783400
C	2.98596000	-0.21016300	-0.99588700
C	3.67828300	2.00049600	0.39741400
C	4.32750000	0.28894300	-0.96702100
N	4.64625400	1.40875300	-0.26150300
H	3.94283100	2.90271500	0.94078500
C	1.25880900	2.17054300	1.18663600
C	1.47555800	3.24126800	2.06192000
N	0.02146900	1.66735000	0.97991600
C	0.38869500	3.80401400	2.72611800
H	2.47172400	3.62943700	2.23309700
C	-1.01671600	2.21296100	1.62398000
C	-0.88513200	3.28509600	2.50336000
H	0.53781000	4.63494400	3.40779600
H	-1.98738600	1.77328200	1.41711200
H	-1.75820400	3.69583500	2.99770600
C	5.34057100	-0.38990300	-1.68772900
C	2.68632600	-1.36308900	-1.76021700
H	6.34705800	0.01159500	-1.64725500
H	1.65847100	-1.70116900	-1.81085300
C	5.02651100	-1.51673100	-2.41300600
C	3.69328500	-1.99932500	-2.45117000

H	5.79850900	-2.03757800	-2.96994000
H	3.46344200	-2.87889800	-3.04404500
H	0.04624700	0.12518800	-1.92274000
H	-5.55351000	-1.62784200	-0.12548000

E = -2971.506620

[4]$^{+}$ (third proton addition to N3′, [N3-H & N2-H & N3′-H]$^{+}$)

1 2

C	-0.91194300	-2.39807300	1.08809200
C	-0.88307800	-3.71688000	1.56766400
C	0.25321800	-4.18788500	2.20924600
C	1.35529600	-3.33879700	2.35207100
C	1.26478100	-2.05406000	1.83818400
N	0.16466900	-1.57980500	1.22278100
H	0.28581400	-5.20521900	2.58544200
H	-1.73259700	-4.37403200	1.42390100
H	2.26274800	-3.66606400	2.84642700
H	2.09783000	-1.36311300	1.91782800
Cu	-0.09250100	0.16983500	0.22905800
C	-2.06499100	-1.79075300	0.40631200
C	-3.30711100	-2.37485900	0.41868600
N	-1.82111000	-0.58129500	-0.22302700
N	-4.35940400	-1.77079500	-0.20716600
H	-3.52053800	-3.30727400	0.92156300
C	-2.90705200	0.04055600	-0.83249300
C	-4.20452900	-0.53943100	-0.84443200
C	-5.27611100	0.09870500	-1.46878400
C	-2.74621000	1.28094100	-1.47132400
H	-1.76082900	1.73483800	-1.46366100
H	-6.25693900	-0.36919300	-1.46261000
C	-3.81559800	1.91895000	-2.09246100
C	-5.08317000	1.32951300	-2.09423600
H	-3.66135400	2.87626500	-2.57941300
H	-5.91798600	1.82245600	-2.58048000
N	1.64932300	0.75285600	-0.80718400
C	2.18151000	1.87766200	-0.03551700
C	2.64846800	-0.24922300	-1.16727100
C	3.51074900	2.12754600	-0.03081000
C	4.01540400	0.07445500	-1.16890200
N	4.40690000	1.34041000	-0.70842700
H	3.93405000	2.93956800	0.54714400
C	1.18569800	2.65696300	0.69851700
C	1.39736300	3.96837500	1.15466300

N	-0.00112300	2.02987000	0.90925300
C	0.39258200	4.61671700	1.85910100
H	2.32978600	4.47747000	0.93941400
C	-0.97410800	2.67638400	1.57754400
C	-0.82253800	3.96093300	2.07888300
H	0.54624200	5.62922800	2.21828700
H	-1.90301300	2.12923900	1.70110400
H	-1.63616500	4.43744300	2.61315600
C	4.95374700	-0.86842800	-1.59564900
C	2.23950100	-1.51069600	-1.58675200
H	6.00981200	-0.61286300	-1.59326800
H	1.18065000	-1.74864400	-1.57980000
C	4.53151200	-2.12290600	-2.03330700
C	3.17557400	-2.44784800	-2.03037200
H	5.26682300	-2.84457800	-2.37342400
H	2.84353800	-3.42223300	-2.37172800
H	1.26601000	1.12788500	-1.67883300
H	5.39240600	1.50803700	-0.57344300
H	-5.27233600	-2.20027300	-0.18380800

E = -2972.146441

[4]$^{+}$ (third proton addition to N2′, [N3-H & N2-H & N2′-H]$^{+}$)

1 2

C	-2.21961900	-1.56276600	-1.33641700
C	-2.97503900	-2.44014500	-2.14994800
C	-2.35125800	-3.43543400	-2.87361100
C	-0.95310900	-3.55560000	-2.80485800
C	-0.26171700	-2.67528500	-1.99868600
N	-0.85462900	-1.70029700	-1.26130100
H	-2.93413400	-4.10011800	-3.50240200
H	-4.04619400	-2.30520600	-2.22842400
H	-0.41849500	-4.31150000	-3.36754100
H	0.81921500	-2.73557600	-1.92289900
Cu	0.34404100	-0.85930000	-0.05369600
C	-2.84497800	-0.49081500	-0.59929700
C	-4.22732900	-0.41066600	-0.30990000
N	-2.06096000	0.53616100	-0.10333800
N	-4.80619800	0.55784700	0.36707500
H	-4.87655500	-1.21689600	-0.64034900
C	-2.60345900	1.61295600	0.58169000
C	-4.00504600	1.59348600	0.81552900
C	-4.58210500	2.66337600	1.52037600
C	-1.82096000	2.68221200	1.02884900

H	-0.75428300	2.70277800	0.81746600
H	-5.65250600	2.63174800	1.69191700
C	-2.42089700	3.73042700	1.72074400
C	-3.80053200	3.72011900	1.97005200
H	-1.81364600	4.56181100	2.06372600
H	-4.25795100	4.54195300	2.51043500
N	1.71110600	0.64452000	0.11722300
C	2.72917200	0.14981200	1.05881100
C	2.29383700	1.20451400	-1.10808200
C	3.96401800	0.70468500	1.03885700
C	3.57313800	1.77945900	-1.06784400
N	4.32403800	1.64560800	0.10995200
H	4.74128700	0.39876000	1.72801800
C	2.28903800	-0.89348400	1.98339100
C	2.99514900	-1.26276600	3.14122200
N	1.11745900	-1.50165400	1.66197900
C	2.49725500	-2.27260400	3.95072000
H	3.91204700	-0.75284400	3.41244400
C	0.64177600	-2.47653100	2.46157800
C	1.29396500	-2.89896000	3.60910900
H	3.03451200	-2.56378700	4.84758100
H	-0.29855100	-2.92243700	2.15404300
H	0.86938200	-3.68614700	4.22082300
C	4.08643200	2.41520700	-2.20104600
C	1.55192500	1.24623300	-2.28292100
H	5.07856400	2.85662600	-2.16825500
H	0.56998100	0.78381600	-2.30415900
C	3.32322400	2.47772000	-3.36565700
C	2.05920700	1.88910000	-3.41379500
H	3.72533600	2.97900800	-4.23970700
H	1.46844000	1.93050400	-4.32215800
H	1.22871400	1.41365300	0.59323600
H	5.28583300	1.95109700	0.08841000
H	-1.06642900	0.52165000	-0.32935600

E = -2972.112201

[4]$^{+}$ (third proton addition to N1′, [N3-H & N2-H & N1′-H]$^{+}$)

1 2

C	-1.20955300	-2.14870900	1.45126600
C	-1.45310200	-3.11394700	2.46282000
C	-0.41856100	-3.77141200	3.08558900
C	0.93354200	-3.49744600	2.72354900
C	1.16701900	-2.56602100	1.75583100

N	0.12591000	-1.91620300	1.15578600
H	-0.63287000	-4.49943400	3.86005400
H	-2.47237400	-3.32420700	2.75807800
H	1.76065200	-4.00909400	3.19891100
H	2.15460800	-2.29187900	1.40584100
Cu	-0.21750500	0.60264200	-0.13815300
C	-2.20134400	-1.41822800	0.72624400
C	-3.58730000	-1.77836900	0.82164200
N	-1.83174800	-0.38923900	-0.10318700
N	-4.55027100	-1.21633000	0.14882800
H	-3.87731300	-2.58863600	1.48515100
C	-2.83246400	0.18812000	-0.86814500
C	-4.18958100	-0.21640900	-0.73162100
C	-5.18268400	0.41014300	-1.50674400
C	-2.51431100	1.20608800	-1.79073300
H	-1.47267300	1.48992000	-1.92696600
H	-6.20662900	0.07708400	-1.37531800
C	-3.50653400	1.80577200	-2.54791500
C	-4.84942800	1.41223400	-2.40404600
H	-3.24499000	2.58170200	-3.26046500
H	-5.61996000	1.88907000	-3.00045500
N	1.67031500	0.73002900	-0.96003500
C	2.45794100	1.55211800	-0.03070000
C	2.36538800	-0.48306200	-1.40297300
C	3.80465700	1.42633500	-0.00175600
C	3.76782400	-0.55172500	-1.35881300
N	4.47144800	0.50675400	-0.76898300
H	4.41776500	2.01924600	0.66535700
C	1.68602000	2.48341500	0.79183700
C	2.24633900	3.57762400	1.47205300
N	0.35325300	2.23181400	0.85912400
C	1.42834200	4.39283500	2.24068800
H	3.30358700	3.79817400	1.38197400
C	-0.43189400	3.03751300	1.60059800
C	0.05814200	4.12140900	2.31268300
H	1.85033800	5.24127900	2.76970900
H	-1.48758800	2.78649800	1.61440200
H	-0.61358700	4.74083000	2.89518700
C	4.42428600	-1.67801300	-1.86276700
C	1.63824800	-1.54177600	-1.93972600
H	5.50892900	-1.72835100	-1.82519900
H	0.55463000	-1.47393600	-1.97837400
C	3.68797200	-2.72348000	-2.41797800

C	2.29517200	-2.66074900	-2.45720900
H	4.20755700	-3.58848900	-2.81638200
H	1.71992800	-3.47146700	-2.89035000
H	1.50292700	1.29779200	-1.79731800
H	5.46606500	0.39922700	-0.63802200
H	0.31148000	-1.23527200	0.41786500

E = -2972.109798

[4]$^{+}$ (third proton addition to Cu, [N3-H & N2-H & Cu-H]$^{+}$)

1 2

C	-2.94430100	-0.38191100	-1.14966900
C	-4.22930400	-0.61741900	-1.65157600
C	-4.47236500	-1.78347100	-2.37319600
C	-3.42624200	-2.67961600	-2.58621200
C	-2.16990500	-2.36869000	-2.07568300
N	-1.93673200	-1.25609200	-1.36405100
H	-5.46119700	-1.98008100	-2.77433400
H	-5.01909500	0.10953500	-1.50600200
H	-3.57115600	-3.59482800	-3.14866900
H	-1.31167400	-3.01100300	-2.24001600
Cu	-0.08040300	-0.79927200	-0.72565500
C	-2.58870100	0.84257600	-0.39536200
C	-3.57915100	1.61670000	0.27911200
N	-1.30604300	1.19132500	-0.36925100
N	-3.29454900	2.70923400	0.94722300
H	-4.61594800	1.29116100	0.29164800
C	-0.99067200	2.37114800	0.24420100
C	-1.99856900	3.12563800	0.92900800
C	-1.64954300	4.32795300	1.59216000
C	0.33093100	2.88472900	0.19111000
H	1.07341200	2.37861800	-0.41628000
H	-2.43549000	4.86729400	2.10942800
C	0.63688000	4.06654400	0.83103400
C	-0.35171100	4.78471900	1.54917600
H	1.64516000	4.46394100	0.77136800
H	-0.08284500	5.70977600	2.04834400
N	1.74750300	-0.22418700	0.12724700
C	2.04279200	-1.20198700	1.17301100
C	2.87221200	0.06078800	-0.76439400
C	3.32614200	-1.51364400	1.47252500
C	4.18455400	-0.25505700	-0.38021700
N	4.38863900	-0.96349200	0.81334200
H	3.56744200	-2.24407700	2.23415000

C	0.87540700	-1.74170300	1.85516400
C	0.92843900	-2.39140400	3.10288700
N	-0.30702900	-1.56552700	1.21219300
C	-0.23851200	-2.87780600	3.66897000
H	1.87107500	-2.49099500	3.62796000
C	-1.43304800	-2.02843400	1.78409300
C	-1.45358100	-2.69448600	2.99919400
H	-0.20851100	-3.38147400	4.62986000
H	-2.34982400	-1.85949500	1.22886600
H	-2.38971900	-3.04944100	3.41391800
C	5.25758400	0.10254100	-1.20026000
C	2.64855600	0.70780400	-1.97568100
H	6.27010400	-0.14897900	-0.89694400
H	1.62876600	0.89816600	-2.28840600
C	5.02516600	0.77839300	-2.39643500
C	3.72166800	1.07974300	-2.78847100
H	5.86475900	1.05668100	-3.02464900
H	3.53387300	1.59028800	-3.72659100
H	1.48699800	0.65063200	0.59245700
H	5.31228900	-1.32626700	0.99528700
H	0.53242100	-1.27129200	-2.05125800

E = -2972.096529

[5]$^{+}$ (forth proton addition to N2′, [N3-H & N2-H & N3′-H & N2′-H]$^{+}$)

1 1

C	-1.02689600	2.54989500	-0.84410400
C	-1.09834500	3.85351400	-1.36073900
C	-0.04076200	4.35617300	-2.10600600
C	1.08846000	3.55804800	-2.30684900
C	1.10526000	2.29019500	-1.74413800
N	0.08000400	1.78136900	-1.03126500
H	-0.08847900	5.36136300	-2.51218800
H	-1.96636100	4.47137700	-1.16164800
H	1.94114000	3.91275300	-2.87416400
H	1.96728200	1.64190300	-1.85830300
Cu	0.00012900	0.00009400	-0.22218500
C	-2.10506000	1.93016300	-0.07153200
C	-3.39185400	2.34575400	-0.08827000
N	-1.72600700	0.78839500	0.76395600
N	-4.37710200	1.69813300	0.61955200
H	-3.71746100	3.17839100	-0.69927000
C	-2.84137800	-0.10601700	1.05958400
C	-4.15880800	0.38250000	1.05442600

C	-5.21472100	-0.44899600	1.43570400
C	-2.60241100	-1.42599100	1.42677300
H	-1.58316700	-1.79712400	1.41424000
H	-6.23096500	-0.06450900	1.42889100
C	-3.65447600	-2.25550900	1.82266400
C	-4.95853000	-1.76166900	1.82915500
H	-3.45308200	-3.27754300	2.12475100
H	-5.78300700	-2.39787300	2.13370100
N	1.72614600	-0.78856000	0.76386100
C	2.10507100	-1.93013900	-0.07201500
C	2.84157800	0.10576800	1.05965700
C	3.39186400	-2.34564600	-0.08924300
C	4.15902100	-0.38269600	1.05397800
N	4.37726400	-1.69813500	0.61848700
H	3.71733900	-3.17812200	-0.70054200
C	1.02667600	-2.54966700	-0.84444700
C	1.09757100	-3.85360200	-1.36031300
N	-0.07981400	-1.78066200	-1.03210800
C	0.03978300	-4.35625100	-2.10531600
H	1.96532400	-4.47169400	-1.16077100
C	-1.10524600	-2.28946000	-1.74478300
C	-1.08903000	-3.55768300	-2.30667100
H	0.08702300	-5.36171500	-2.51086800
H	-1.96686600	-1.64075100	-1.85961600
H	-1.94188600	-3.91230200	-2.87378000
C	5.21500000	0.44869800	1.43528600
C	2.60263600	1.42557500	1.42747000
H	6.23126700	0.06428100	1.42801500
H	1.58336800	1.79665100	1.41544800
C	4.95885400	1.76120300	1.82933500
C	3.65477800	2.25497900	1.82340900
H	5.78338800	2.39733100	2.13388500
H	3.45341100	3.27687200	2.12599600
H	1.39486000	-1.16173700	1.65721100
H	5.33325200	-1.98472400	0.46934700
H	-5.33311800	1.98449900	0.47016600
H	-1.39466100	1.16132600	1.65738800

E = -2972.733377

[5]$^{+}$ (forth proton addition to Cu, [N3-H & N2-H & N3′-H & Cu-H]$^{+}$)

1 3

C	-0.89697700	-1.99430900	1.39171800
C	-0.86382900	-2.98025700	2.38800300

C	0.35306500	-3.34062600	2.95291900
C	1.51740400	-2.70919100	2.51500400
C	1.40513000	-1.73921800	1.52633200
N	0.23551300	-1.38552600	0.97180200
H	0.39152700	-4.10355300	3.72366200
H	-1.77249700	-3.46397000	2.72494600
H	2.48823200	-2.95991700	2.92673700
H	2.28263200	-1.22436600	1.15104100
Cu	-0.10849600	0.06693000	-0.55428000
C	-2.13610700	-1.54435000	0.72293100
C	-3.36632200	-2.09236200	1.02050000
N	-1.99321100	-0.55763800	-0.21422500
N	-4.48453600	-1.64311200	0.38447600
H	-3.51194000	-2.88385500	1.74059300
C	-3.12815700	-0.10978500	-0.86971300
C	-4.41608600	-0.63964900	-0.57715300
C	-5.55824500	-0.17300400	-1.23015100
C	-3.04036500	0.89758400	-1.84866500
H	-2.05617300	1.27295700	-2.09900900
H	-6.52919400	-0.59518600	-0.98613400
C	-4.17879200	1.35885400	-2.49592900
C	-5.43906100	0.82810700	-2.18921200
H	-4.08821000	2.13283900	-3.25076800
H	-6.32473700	1.19122400	-2.69928600
N	1.89255200	0.78716800	-0.87750800
C	2.25509100	1.71016500	0.19130400
C	2.94270200	-0.15940600	-1.24636200
C	3.55244900	1.87321900	0.54092800
C	4.27784400	0.07358900	-0.87431100
N	4.56877200	1.17870900	-0.06103900
H	3.84463000	2.53847500	1.34356900
C	1.13527600	2.41178900	0.81596200
C	1.28310900	3.58209400	1.58285000
N	-0.08938100	1.87605500	0.59428200
C	0.16244800	4.17424200	2.14533100
H	2.26013000	4.03268000	1.71352100
C	-1.16744900	2.46765800	1.13455500
C	-1.09652600	3.60885100	1.92104100
H	0.26453100	5.07773800	2.73814000
H	-2.12113200	1.99846400	0.91445000
H	-1.99774000	4.04897000	2.33185100
C	5.28010600	-0.80573100	-1.29184800
C	2.62748600	-1.26739200	-2.02812200

H	6.31039500	-0.62028300	-1.00043000
H	1.59132000	-1.42084400	-2.30923600
C	4.95720400	-1.90378000	-2.08781600
C	3.63272500	-2.13734100	-2.45610500
H	5.74420600	-2.57500100	-2.41549000
H	3.37751000	-2.98931900	-3.07688300
H	-0.24362100	-0.05717700	-2.09630300
H	1.64122300	1.32198300	-1.71123900
H	5.50375500	1.26709200	0.30601300
H	-5.38112700	-2.05803200	0.59589800

E = -2972.694270

[6]$^{+}$

1 2

C	-0.84573000	-1.88002700	1.59176700
C	-0.72804100	-2.90506200	2.54849000
C	0.51011900	-3.17650200	3.10840500
C	1.61513400	-2.40630800	2.73118700
C	1.42071300	-1.39779300	1.79976500
N	0.23130300	-1.13703500	1.22853600
H	0.61286200	-3.96635700	3.84567700
H	-1.60301400	-3.46177700	2.86295700
H	2.59689400	-2.57626800	3.15743900
H	2.24439000	-0.76746600	1.48300800
Cu	-0.17328700	0.14562200	-0.38737800
C	-2.10108400	-1.52143400	0.94475600
C	-3.20093400	-2.30944500	0.90246700
N	-2.12393200	-0.19178100	0.34322000
N	-4.36443100	-1.91731900	0.30087700
H	-3.19618600	-3.30792100	1.32059700
C	-3.25134800	0.04922200	-0.55415100
C	-4.38112800	-0.78234500	-0.52324100
C	-5.48391800	-0.49087100	-1.33003800
C	-3.22961600	1.14683900	-1.40778400
H	-2.33448400	1.75544000	-1.45791800
H	-6.35443200	-1.14037600	-1.30121300
C	-4.33714000	1.44803900	-2.20286500
C	-5.46416600	0.62823900	-2.15979900
H	-4.31071100	2.31148100	-2.85852600
H	-6.32724200	0.84992700	-2.77864500
N	1.80800600	0.64356600	-0.99292400
C	2.35525100	1.62650800	-0.06642900
C	2.72117000	-0.44141800	-1.34780100

C	3.68439400	1.65730800	0.19406100
C	4.09552800	-0.34135700	-1.07465800
N	4.56622600	0.77869900	-0.37283700
H	4.10644100	2.36313200	0.89817900
C	1.38058900	2.54476900	0.51918800
C	1.73698200	3.77888000	1.09531800
N	0.08314100	2.15590100	0.45044700
C	0.75186500	4.59529600	1.62859900
H	2.77109300	4.10301400	1.09834500
C	-0.85972600	2.97294800	0.94918300
C	-0.58439600	4.19013900	1.55517600
H	1.01674600	5.54815400	2.07561200
H	-1.88886900	2.64008800	0.83891900
H	-1.38853900	4.80714100	1.93877600
C	4.96206300	-1.35994400	-1.47760500
C	2.23197000	-1.55740700	-2.02029100
H	6.02382500	-1.27547500	-1.26242700
H	1.16848200	-1.61098900	-2.22655200
C	4.46531500	-2.46799400	-2.16239300
C	3.10169600	-2.56883500	-2.43432100
H	5.14767500	-3.24954600	-2.47974600
H	2.71048900	-3.42763100	-2.96887400
H	-0.54841400	-0.13193500	-1.85643800
H	1.52705200	1.11619100	-1.85424300
H	5.52997800	0.78971900	-0.07693600
H	-5.10346100	-2.59445900	0.18750600
H	-2.17082600	0.48998600	1.10531800

E = -2973.287686

$[Cu(H_2O)_4]^+$ + 2pqH_2

1 1

C	-2.20617700	2.23738800	-1.43662800
C	-2.42486900	3.42465800	-2.16985000
C	-1.35058900	4.13257400	-2.67876900
C	-0.05117300	3.65430900	-2.47207200
C	0.09237900	2.47192500	-1.76592300
N	-0.94273500	1.77321800	-1.26108600
H	-1.52081700	5.04512400	-3.24139900
H	-3.43182000	3.77843100	-2.35318000
H	0.81753300	4.17797600	-2.85340500
H	1.07788700	2.05510700	-1.57504800
C	-3.30686900	1.47201600	-0.85280900
C	-4.58885200	1.90838200	-0.80770200

N	-3.00595100	0.21891900	-0.20481300
N	-5.59620500	1.14306600	-0.25540100
H	-4.88415300	2.88148000	-1.17309500
C	-4.08567600	-0.72571100	-0.14020200
C	-5.40564900	-0.24531000	-0.10975400
C	-6.46656300	-1.13335300	0.04760700
C	-3.84757100	-2.09064300	-0.01859200
H	-2.82459600	-2.45667200	-0.05071300
H	-7.48508600	-0.75494600	0.06048700
C	-4.91450200	-2.98234600	0.15038200
C	-6.22003400	-2.50305200	0.18789500
H	-4.71613000	-4.04401300	0.25212300
H	-7.05276600	-3.18575600	0.31869700
N	3.16198400	-0.42096400	0.52414100
C	3.85937700	-1.15744700	-0.46659500
C	3.42319200	0.95400000	0.63582000
C	5.07180900	-0.68360800	-0.85400600
C	4.68241100	1.43695300	0.23449500
N	5.57273300	0.49773400	-0.33400700
H	5.69876900	-1.19081000	-1.57320700
C	3.22942000	-2.35596500	-1.00213800
C	3.86812300	-3.22004400	-1.91950600
N	1.96209000	-2.62090000	-0.57791500
C	3.19549800	-4.32378100	-2.40931100
H	4.88358000	-3.02378300	-2.24186600
C	1.32404800	-3.70608600	-1.06853000
C	1.88264600	-4.57952500	-1.98362800
H	3.68411300	-4.98687000	-3.11624900
H	0.31867300	-3.86828700	-0.68664100
H	1.32372600	-5.43499900	-2.34444700
C	4.98699400	2.78359300	0.39233800
C	2.47493800	1.83089700	1.15140200
H	5.96015500	3.15530700	0.08282100
H	1.50821600	1.39857100	1.40506000
C	4.04438200	3.65874700	0.95462900
C	2.79007500	3.18599700	1.32429500
H	4.30031500	4.70440000	1.08774000
H	2.05141100	3.86571500	1.73844300
H	2.19832100	-0.66999100	0.69335700
H	6.42726700	0.85726100	-0.73194200
H	-6.54490400	1.47049600	-0.35819400
H	-2.16346800	-0.21236900	-0.57456000
Cu	0.09521000	-0.33527200	1.94177500

O	-0.03793500	-0.39336800	-0.01004100
H	0.54067700	-0.97410600	-0.53509100
O	0.24221400	0.80229700	3.53673100
H	-0.65304900	1.13567500	3.70421900
O	0.77702800	-2.30101800	1.96387900
H	1.24972600	-2.70719600	2.70141800
O	-2.06280200	0.00090400	2.46034600
H	-2.45693900	0.22975400	1.58121700
H	-2.65362900	-0.66505000	2.83775400
H	0.86698900	1.53268300	3.63543500
H	-0.32975000	0.42776300	-0.52782800
H	1.29662000	-2.49345600	1.14576500

E = -3278.453472

[Cu(pqH$_2$)(H$_2$O)$_2$]$^+$ + pqH$_2$

1 1

C	3.34728600	2.56290200	0.06214900
C	4.12379500	3.72400200	-0.06517500
C	3.63010100	4.94014300	0.38598900
C	2.34894100	4.98431600	0.94200900
C	1.61687000	3.80854700	1.00483800
N	2.08342300	2.61458400	0.57860400
H	4.22614400	5.84202900	0.29209500
H	5.09849600	3.66887500	-0.53617300
H	1.91762100	5.91139300	1.30180900
H	0.61159700	3.80018800	1.41108500
Cu	1.12622100	0.99282800	0.45979700
C	3.82723600	1.23533800	-0.33173400
C	5.13300900	0.89055500	-0.35542300
N	2.80657300	0.24841100	-0.62594000
N	5.54122800	-0.39726900	-0.64532700
H	5.91765300	1.58866000	-0.09223500
C	3.24609700	-1.12052300	-0.50859400
C	4.61468900	-1.44657000	-0.55210000
C	5.01592900	-2.78197800	-0.48183200
C	2.30793800	-2.14490600	-0.38632800
H	1.25186000	-1.89030900	-0.38297600
H	6.07447700	-3.02505000	-0.52039600
C	2.70786500	-3.48559800	-0.33121600
C	4.06395600	-3.79888800	-0.37804900
H	1.95932900	-4.26720600	-0.25534600
H	4.39064000	-4.83262300	-0.33415600
N	-2.40028100	-1.38793300	0.42845400

C	-3.60107500	-0.99504600	-0.27511000
C	-2.19936400	-2.80217800	0.60404700
C	-4.24648500	-1.90361200	-1.03748700
C	-2.90233800	-3.71958000	-0.19868300
N	-3.83136700	-3.22014700	-1.12630800
H	-5.08383500	-1.62466500	-1.66265700
C	-4.00949100	0.41438400	-0.19446100
C	-5.35911100	0.79301100	-0.32695100
N	-3.04742100	1.34212500	0.03182200
C	-5.70445300	2.13566600	-0.26293100
H	-6.12261800	0.03235400	-0.44398400
C	-3.40144200	2.63644300	0.11414900
C	-4.70610600	3.08677700	-0.03284600
H	-6.73405700	2.46294100	-0.36225600
H	-2.58913300	3.33555900	0.29909900
H	-4.95958700	4.13781700	0.03714100
C	-2.66083000	-5.08528200	-0.05955400
C	-1.27253000	-3.26960400	1.52993200
H	-3.21346600	-5.78876500	-0.67648900
H	-0.73154200	-2.54963100	2.13818700
C	-1.72319900	-5.54814900	0.86857300
C	-1.03095300	-4.64266300	1.66622100
H	-1.54773800	-6.61436400	0.96542300
H	-0.30925400	-4.99261500	2.39697700
H	-2.34058400	-0.90297600	1.32168400
H	-4.43212900	-3.88178800	-1.59269000
H	6.51411700	-0.62522200	-0.50746400
H	2.39390900	0.41288600	-1.56016100
O	-7.40661500	4.86328900	-0.21862700
H	-7.94213700	5.19170100	0.51458900
H	-7.73240000	5.34764000	-0.98772500
O	1.03483500	0.85225100	-2.75945400
H	0.28859000	0.69146600	-2.15023000
O	0.94266000	-0.51244200	2.02827500
H	1.15783600	-0.24025200	2.93040900
O	-0.55102800	0.44006800	-0.47756100
H	-0.93172500	-0.45121000	-0.27928300
H	0.82392600	0.39129700	-3.58015400
H	1.54872200	-1.24239000	1.82087900
H	-1.38702900	0.97349700	-0.30592400

E = -3278.460559

TS (from intermediate **[6]**•)

1 2

C	3.54830900	0.30085000	0.55201500
C	4.91136600	0.35219200	0.89249100
C	5.48982900	-0.71562700	1.56375600
C	4.70930900	-1.83611200	1.86707000
C	3.37902300	-1.83162400	1.47270300
N	2.79892100	-0.79827300	0.83215200
H	6.54011800	-0.68323100	1.83480200
H	5.50933100	1.21373700	0.61982000
H	5.12315500	-2.69557800	2.38153600
H	2.73484900	-2.68364000	1.66817400
Cu	0.83887800	-0.57487800	0.42312800
C	2.84220800	1.39538200	-0.11194200
C	3.27220100	2.67756600	-0.11783700
N	1.58530000	1.03554800	-0.76423500
N	2.56251700	3.68895600	-0.71814800
H	4.17943400	2.97897100	0.38935300
C	0.72081600	2.16699400	-1.06352300
C	1.22658200	3.47927600	-1.07962600
C	0.38948800	4.54362700	-1.42874300
C	-0.61075100	1.94237700	-1.39759300
H	-0.98708800	0.92453800	-1.38697800
H	0.78745900	5.55422500	-1.43258600
C	-1.44370100	3.00269500	-1.76653900
C	-0.93955500	4.30309100	-1.77836200
H	-2.47586100	2.80860700	-2.03822700
H	-1.57744500	5.13630100	-2.05558000
N	-2.08138700	-0.92991400	0.76318100
C	-2.25144500	-1.70594200	-0.35110700
C	-3.11410700	-0.12117800	1.20162200
C	-3.44655000	-1.68031100	-1.04147300
C	-4.35158900	-0.08106400	0.50546900
N	-4.46774400	-0.88596500	-0.62127400
H	-3.62334400	-2.25555100	-1.93830800
C	-1.14301600	-2.57662400	-0.80400500
C	-1.43500200	-3.79322000	-1.43998200
N	0.13795700	-2.17584300	-0.58553700
C	-0.40397500	-4.60114500	-1.90112000
H	-2.46416700	-4.11289200	-1.54750800
C	1.12527100	-2.98104500	-1.03573500
C	0.90956900	-4.18067800	-1.69822600
H	-0.62241900	-5.54229900	-2.39405800
H	2.13545500	-2.63533600	-0.85240000

H	1.75431600	-4.77145800	-2.03300600
C	-5.39694900	0.73432200	0.94697400
C	-2.96290400	0.67186200	2.35365600
H	-6.33424300	0.75040600	0.39969500
H	-2.02437700	0.63649200	2.89381900
C	-5.22088300	1.51534700	2.08544000
C	-4.00623900	1.48206700	2.78543400
H	-6.03104800	2.14875300	2.43020400
H	-3.87834600	2.09033200	3.67464000
H	-0.02762300	-0.21817200	1.70828100
H	-0.92559600	-0.63945500	1.16312700
H	-5.32858600	-0.86900600	-1.15280000
H	2.86500100	4.63901700	-0.56062600
H	1.81076800	0.57667800	-1.64996600

E = -2973.329527