Formate Dehydrogenase Activity by a Cu(II)-based Molecular Catalyst and Deciphering the Mechanism by DFT studies

SUPPORTING INFORMATION

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Materials and methods

Commercially available reagent-grade compounds were employed in this study. No additional purification was required for the chemicals purchased from Sigma Aldrich or Alfa Aesar for synthesis purposes. Merck supplied all of the analytical-grade solvents that were filtered and dried before use in this project. All experiments were conducted using milli-Q water.

NMR Spectroscopy. At room temperature, Bruker Ultrashield NMR spectrometer (400 MHz) was used to record ^{1}H and ^{13}C NMR spectra using tetramethylsilane as an internal standard.

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. The experimental parameters are listed as follows.

S.N.[#]	Microwave		Modulation		Temperature (K)
	Frequency GHz	Power mW	Frequency kHz	Amplitude G	
1	9.455	2.52	100	1.98	120
2	9.45	2.01	100	1.98	120
3	9.5	2.01	100	2.08	120
4	9.44	2.01	100	2.08	120

[#] 1. Frozen MeOH and toluene for [Cu(N3Q3)Cl]Cl complex.
2. Frozen MeOH and toluene for [Cu(N3Q3)Cl]Cl complex in the presence of HCOOH and HCOONa.
3. Frozen water for $[Cu(N3Q3)Cl]^+$ complex.
4. Frozen water for $[Cu(N3Q3)Cl]^+$ complex in the presence of HCOOH and HCOONa after heated at 70 ℃.

Mass Spectrometry. Waters Micromass Q-Tof Micro and Bruker MICROTOF-Q11 systems recorded high-resolution ESI mass spectra.

X-ray crystallographic analysis. A Bruker APEX-II CCD diffractometer single-crystal X-ray diffractometer was used to gather the single-crystal X-ray diffraction data of the single crystal of copper complex. The CrysAlisPro programme was used to gather and analyse data for the research. The images were captured using an EosS2 CCD detector and processed using CrysAlisPro software. Crystal data were acquired at 293 K using CrysAlisPro (Rigaku Oxford Diffraction, 2017), and the structure was solved using the Charge Flipping solution programme in Olex2 (Rigaku Oxford Diffraction) employing spherical harmonics for empirical absorption correction.

Gas evolution. The gas evolution was established on manometric observations in a 5 mL double-jacketed reaction vessel with a headspace capacity of 3 mL and 2 mL of the reaction mixture. There were 2 mL of water in the reference cell and 3 mL of headspace in the working cell. The ideal gas equation PV= nRT was used to convert the H_2 and CO_2 produced during dehydrogenation into micromoles. A TESTO 521 differential pressure manometer with a measurement range of 0 to 100 hPa and an accuracy of 0.1 hPa was used to gauge the evolved gas pressure.

Gas Detection. The gaseous product was recorded through CIC GC-2011 Gas chromatography through a porapak Q or molecular sieve column with a TCD detector and argon as a carrier gas.

Cyclic Voltammetry. All the electrochemical measurements for complex **[Cu(N3Q3)Cl]Cl** using cyclic voltammetry techniques were performed in CHI1140C

electrochemical workstation under a nitrogen atmosphere with a scan rate of 100 mV s^{-1} in organic and aqueous medium at room temperature. The three electrodes system used **glassy carbon**, **Pt wire**, and **saturated calomel** as working, counter, and reference electrodes throughout the cyclic voltammetric experiments.

Computational method. All density functional theory (DFT) level computations were carried out using Gaussian 09 package [1] with unrestricted B3LYP-D3 functional [2-4]. All geometries were optimized using 6-311+G(d,p) [5,6] basis set for all atoms except Cu, for which effective core potential type LANL2DZ [8-10] basis set was used. The numerical integrals were computed using the Gaussian's ultrafine grid option enabled. The Integral equation formalism polarizable continuum mode model (IEFPCM) [7] was used to account for water solvation medium. Vibrational frequencies under harmonic approximations at 298.15 K, of optimized geometry of all structures were calculated using the same basis set mentioned above, and was used to distiguish between intermediate and transition state (TS) structures. The presence of single imaginary frequency for the stationary states was taken as sign of TS structure and intrinsic reaction calaculation was carried out to corraborate that connections between TS structure and its forward and backward minima [11]. The frequency calulation was also used to obtain the thermal contributions to the free energy of each chemical species. Later, IEFPCM solvated B3LYP-D3 single point calualtions were performed on each species using basis set effective core potential type LANL2DZ for Cu and 6-311+G(2df,p) for other elements, using the previous optimized structure. These single point energies were added to the corresponing thermal contributions to finally arrive at the composite free energies for each chemical species [13]. The 1 M standard state Gibbs free energy of each molecule was calculated by adding entropy penalty required to change concentration from 1/24.5 M to 1 M (1.89 kcal/mol at 298.15 K) to the previously obtained values [14]. Gauss View 5.0.9 program [12] was used for input file preparation, visualization and analysis purposes.

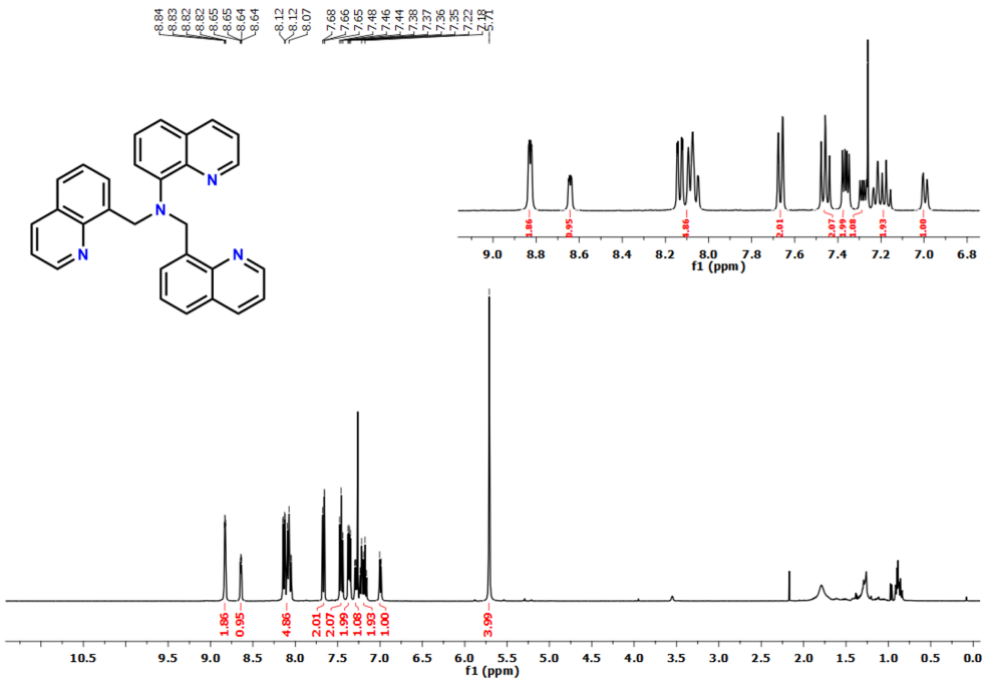


Figure S1. ^{1}H NMR of N3Q3 ligand in CDCl3.

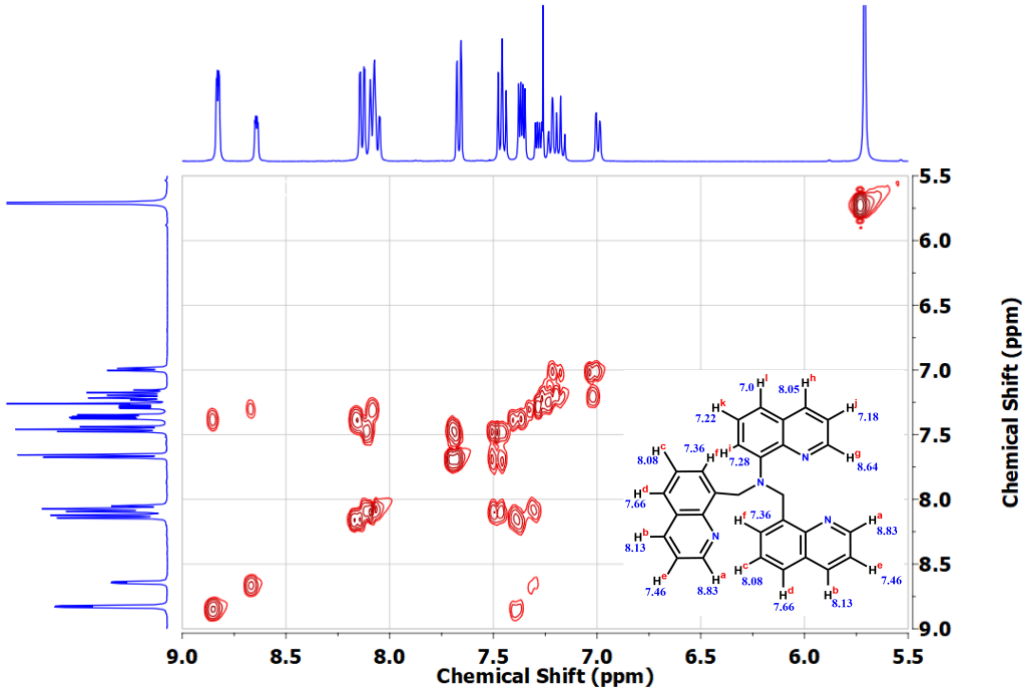


Figure S2. ^{1}H-^{1}H COSY NMR spectrum of N3Q3 ligand in $CDCl_3$.

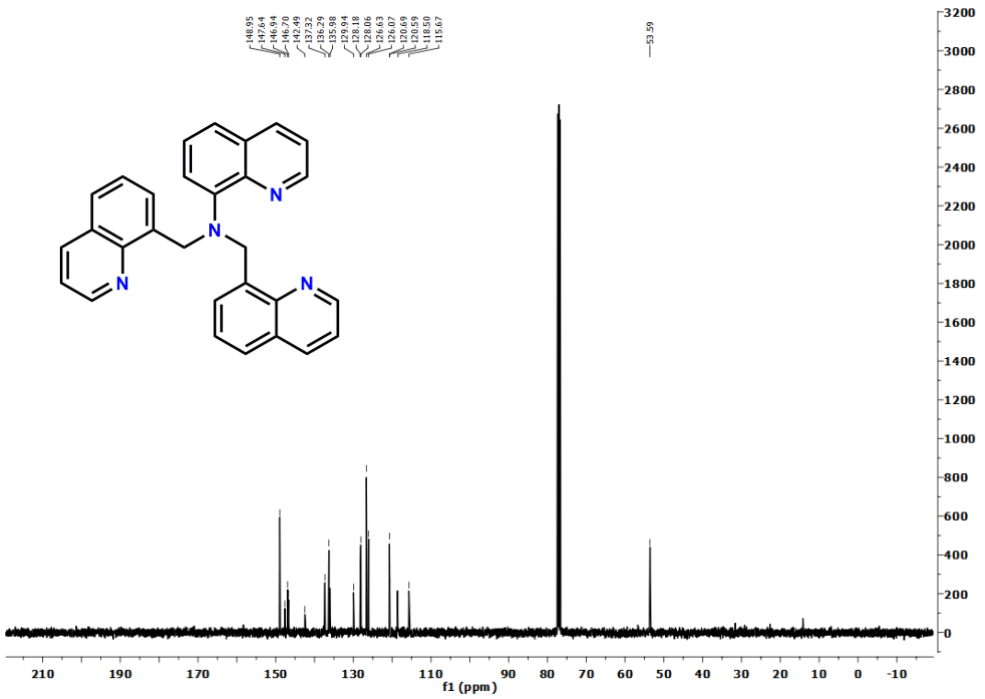


Figure S3. ^{13}C NMR of N3Q3 ligand in $CDCl_3$.

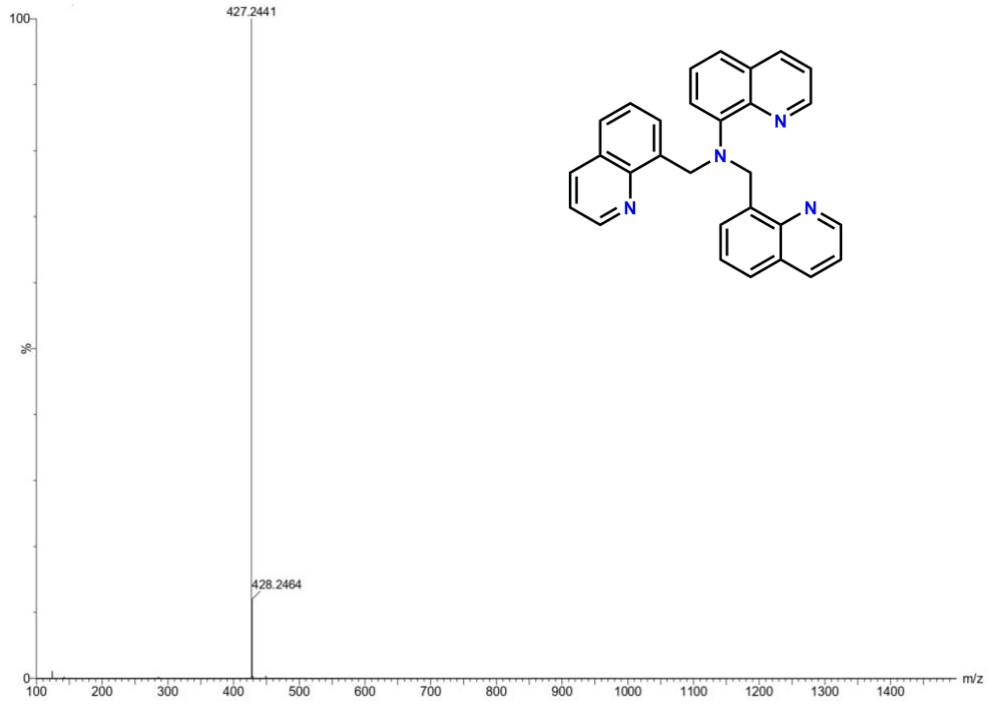


Figure S4. ESI-HRMS spectra of N3Q3 ligand in methanol for $[M+H]^+$ m/z.

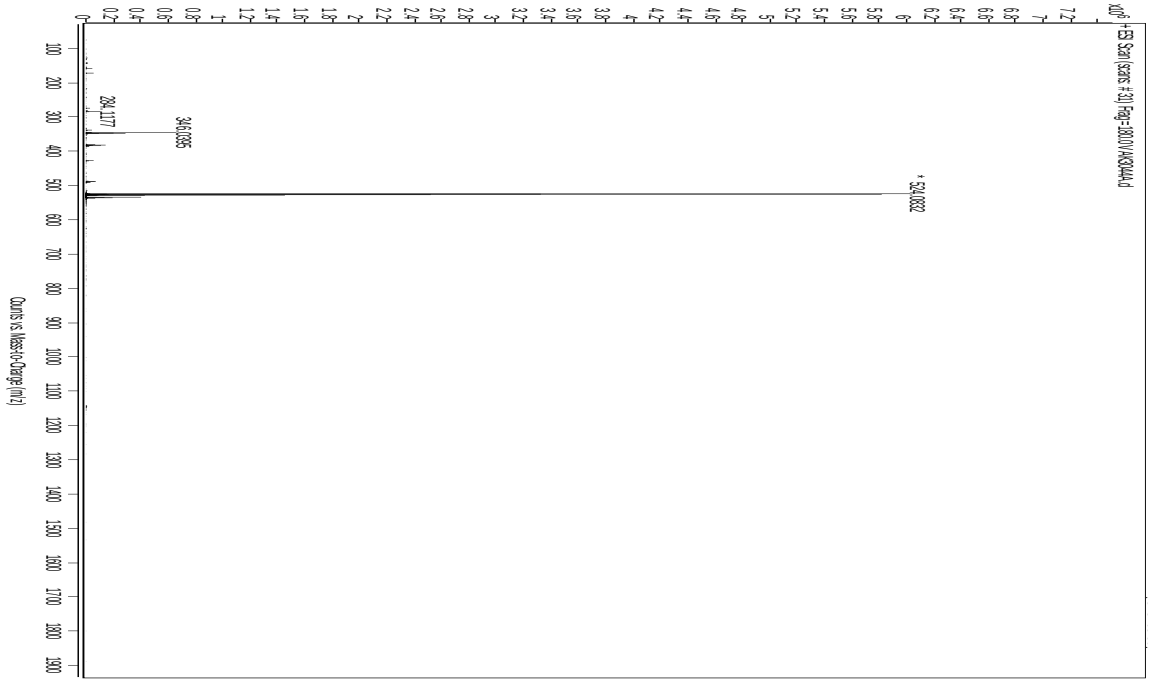


Figure S5. ESI-HRMS spectra of [Cu(N3Q3)Cl]Cl complex in methanol for $[C_{29}H_{22}CuClN_4]^+$ i.e. $[Cu(N3Q3)Cl]^+$.

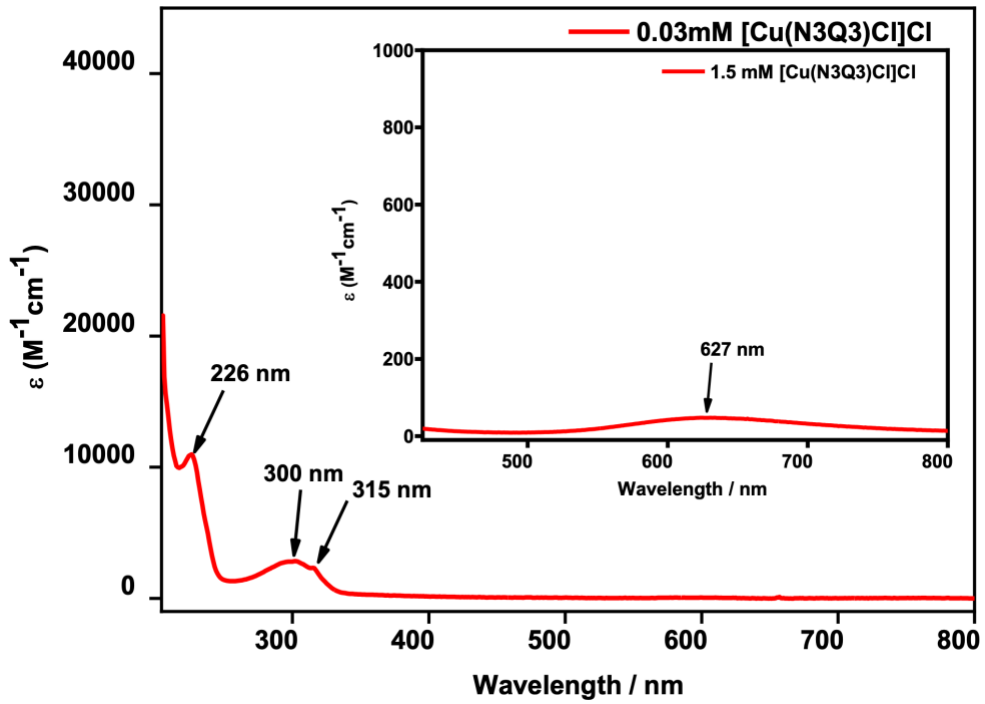


Figure S6. The UV-Vis spectrum of [Cu(N3Q3)Cl]Cl complex in methanol.

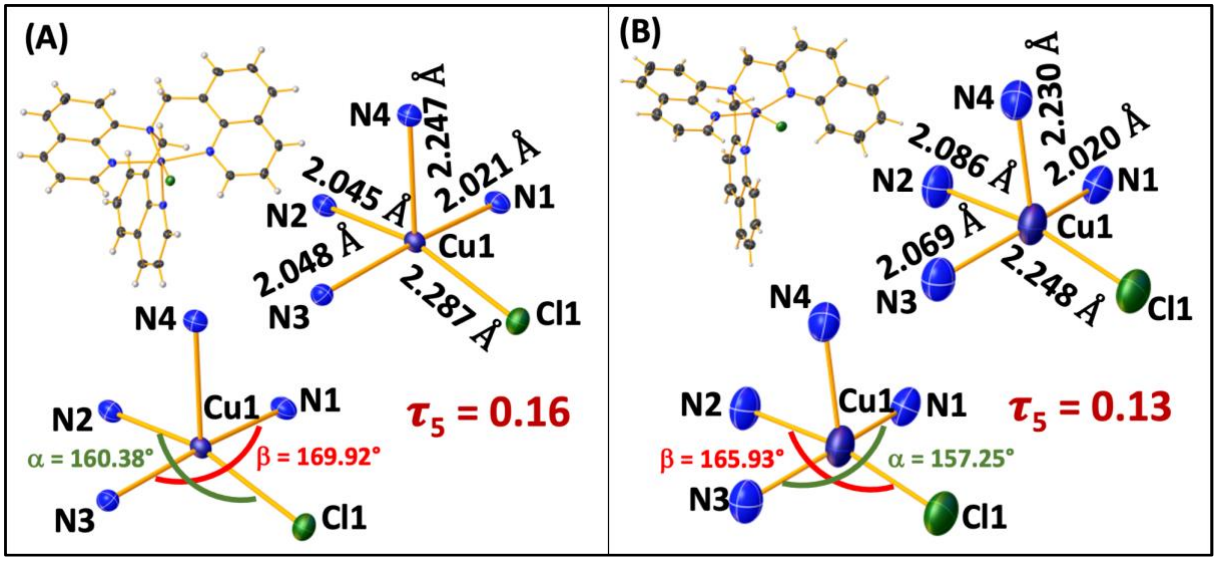


Figure S7. The geometrical structure and parameters of $[Cu(N_3Q_3)Cl]^+$ and $[Cu(o\text{-}N_3Q_3)Cl]^+$ (*Spectrochim Acta A Mol Biomol Spectrosc* **2014**, *130*, 390–396).

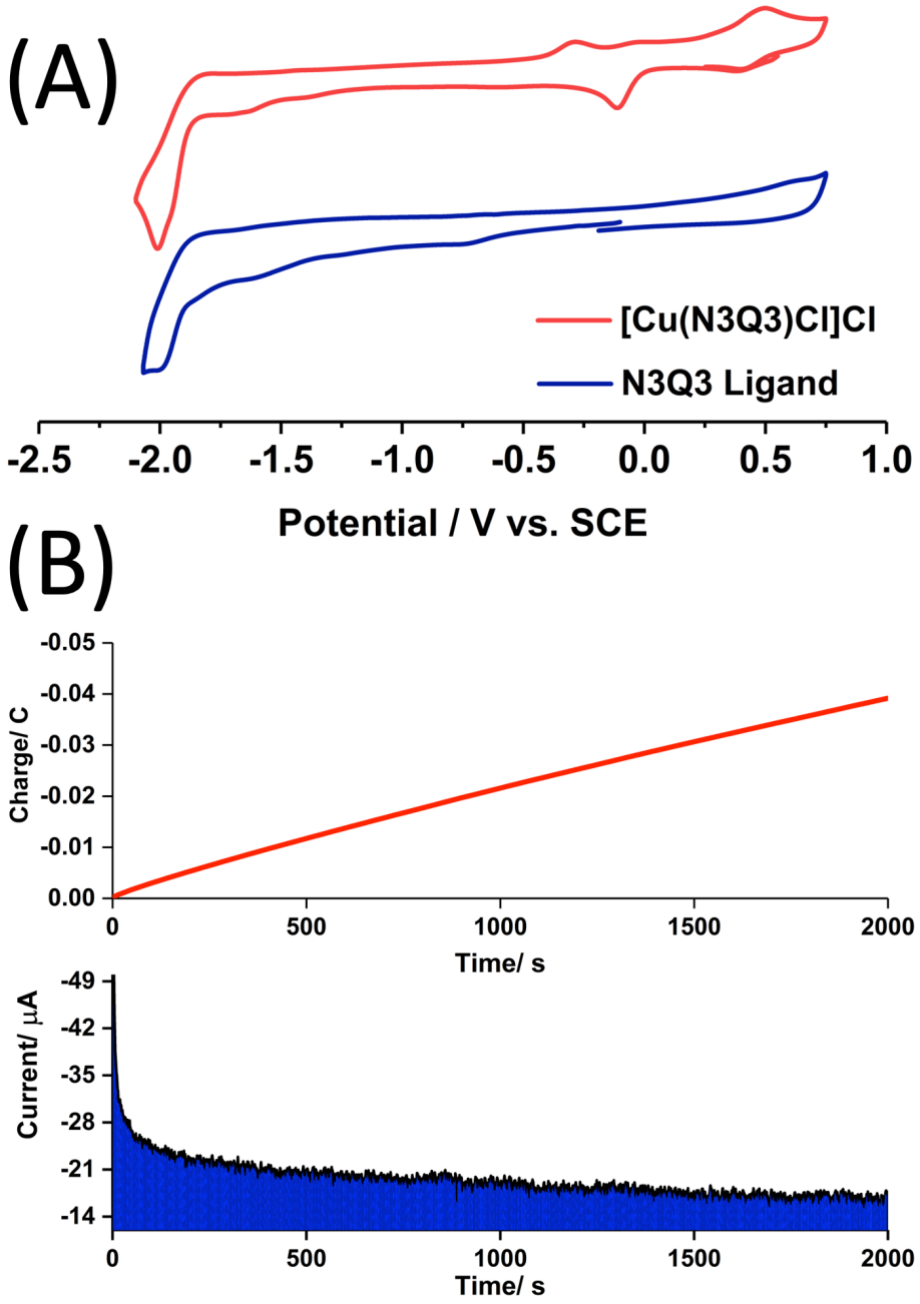


Figure S8. (A) Cyclic voltammogram of 1.0 mM [Cu(N3Q3)Cl]Cl complex (Top) and 1.0 mM N3Q3 ligand. Electrolytic condition: 0.1 M TBAP as supporting electrolyte in DMF medium at a scan rate of 100 mV s^{-1} using a three-electrode system. **(B)** The coulometry of [Cu(N3Q3)Cl]Cl (Electrocatalytic condition: 0.20 µmol of the complex in 5 mL of 0.1 M $^{n}Bu_4NClO_4$ as supporting electrolyte). TOP: Charge consumed at 2000 s, Bottom: Current vs. Time plot.

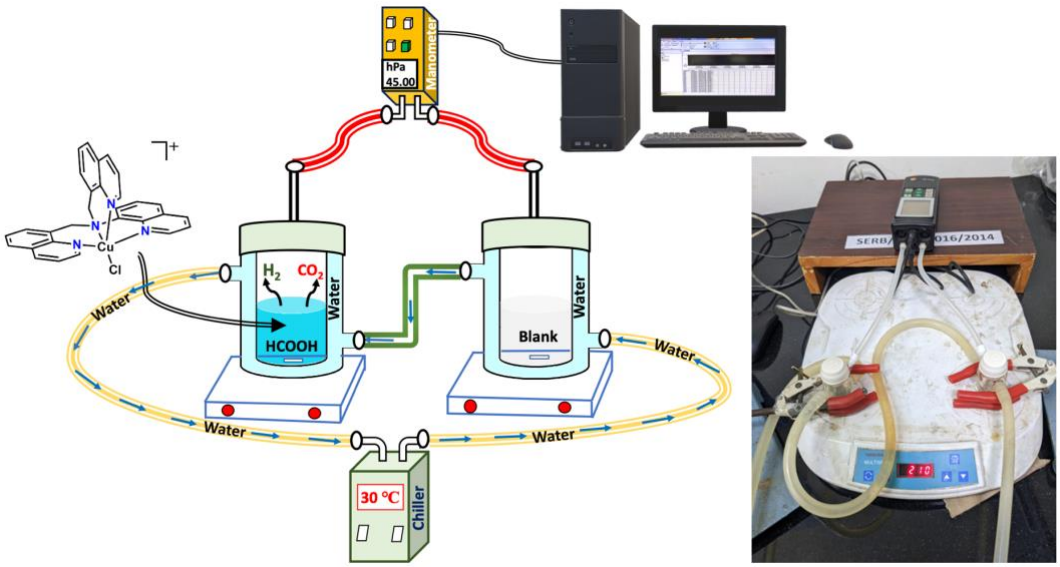


Figure S9. A general diagram for the reaction set-up.

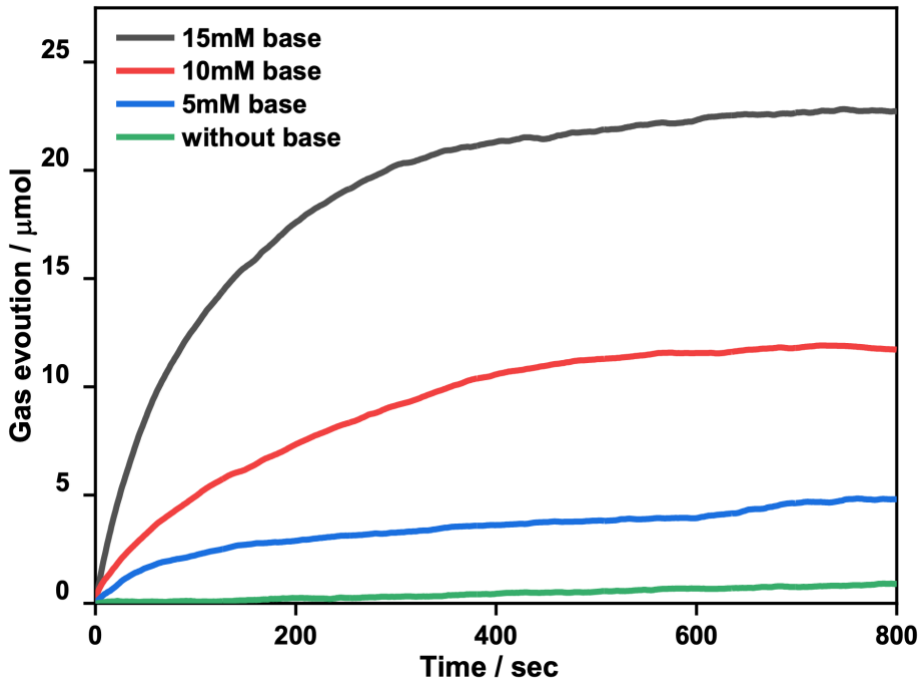


Figure S10. Gas evolution by [Cu(N3Q3)Cl]Cl complex at 50 °C in water with various base concentrations in the presence of 1.0 mM of complex and 15 mM of the acid

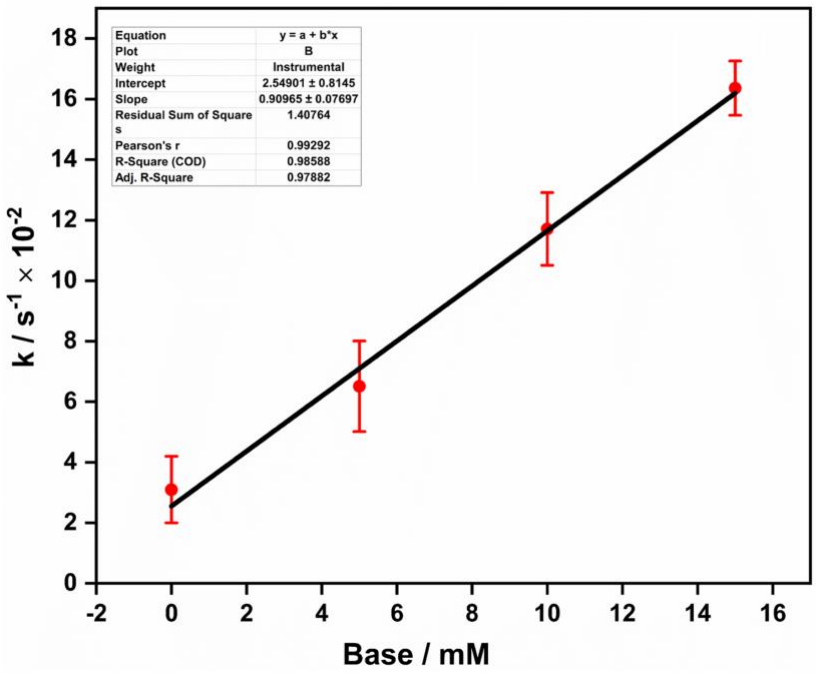


Figure S11. Rate of gas evolution *vs.* base in water.

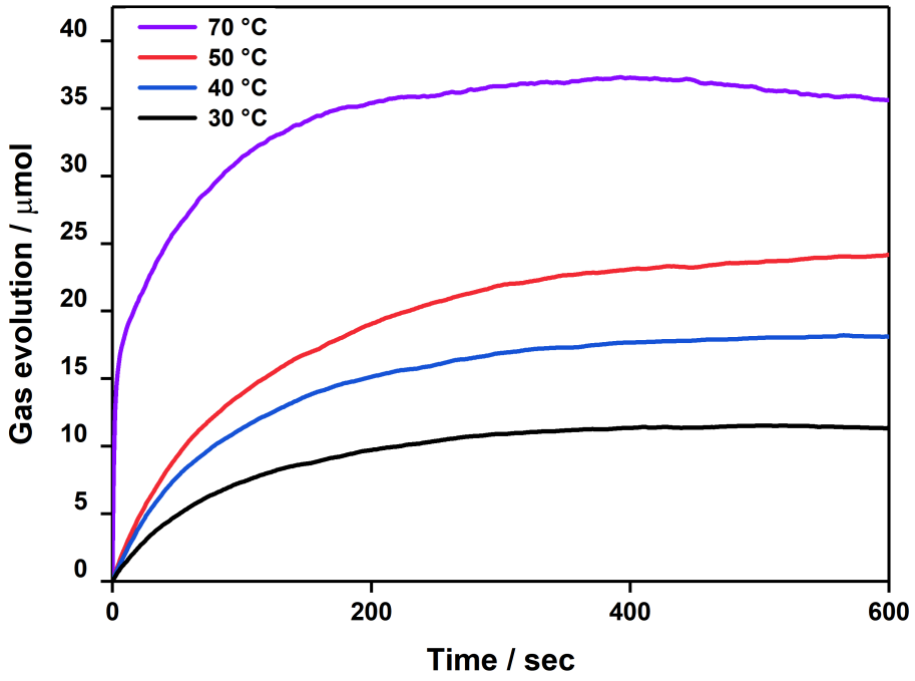


Figure S12. Gas evolution by [Cu(N3Q3)Cl]Cl complex with temperature variation in the presence of 1.0 mM of complex, 15 mM of the acid and 15 mM of the base.

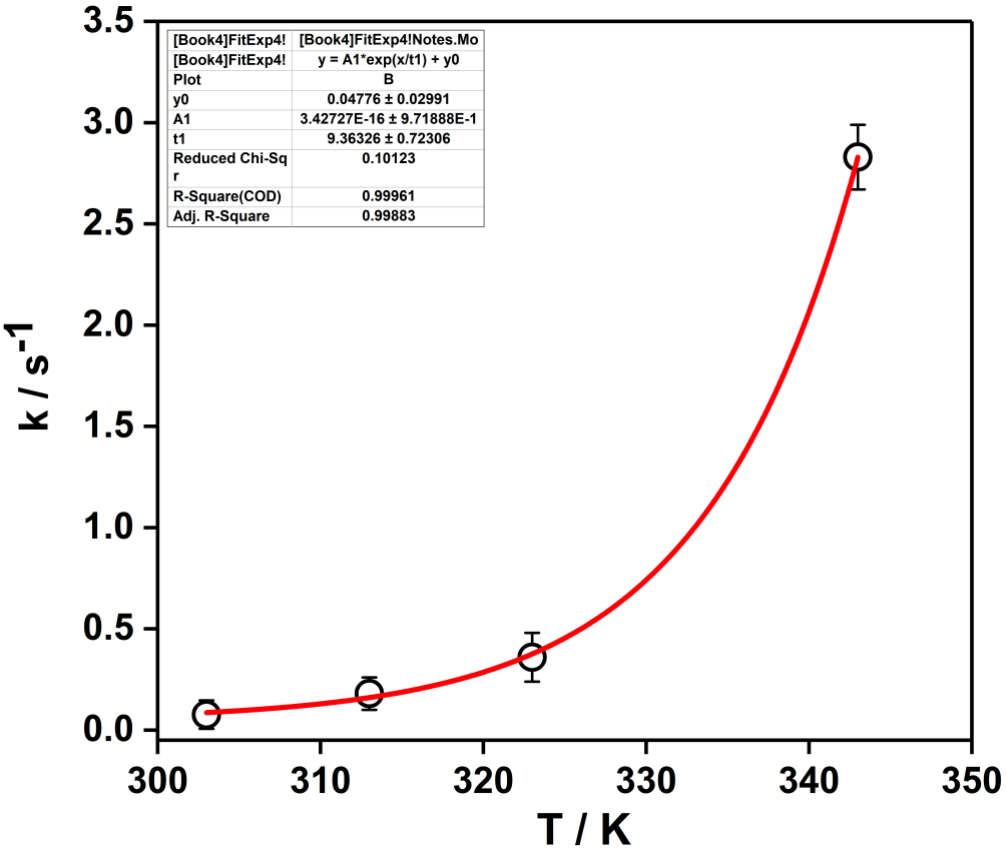
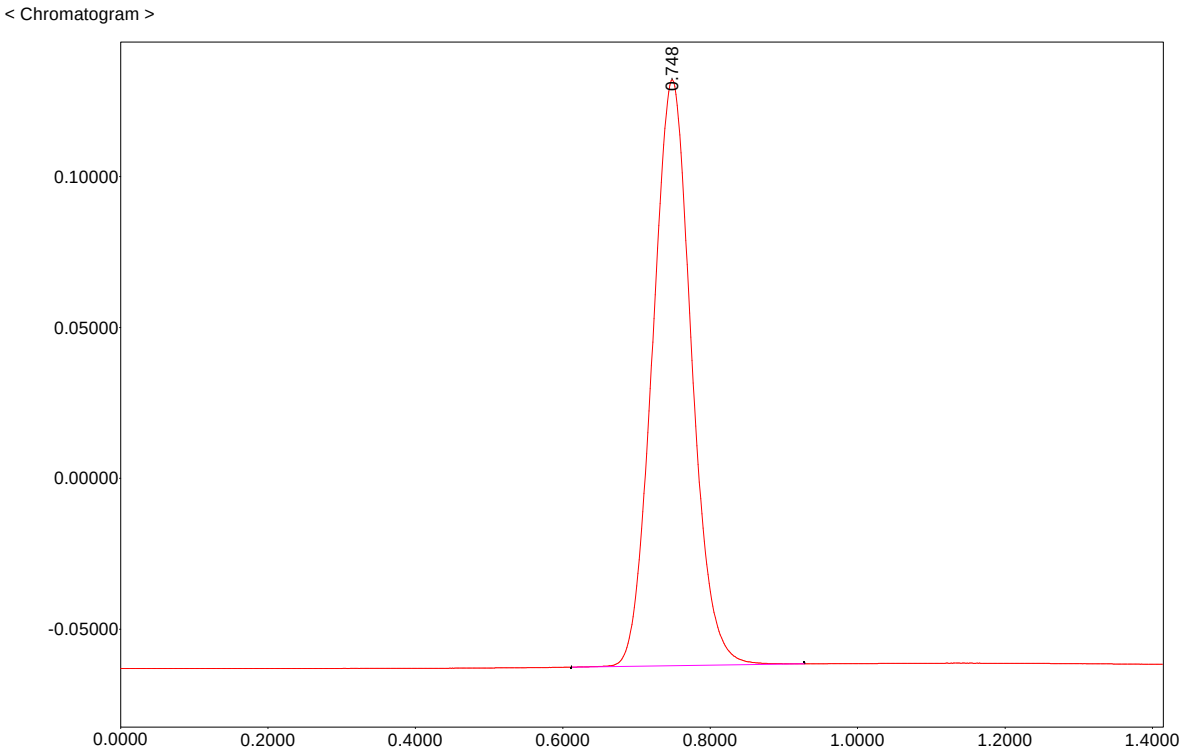


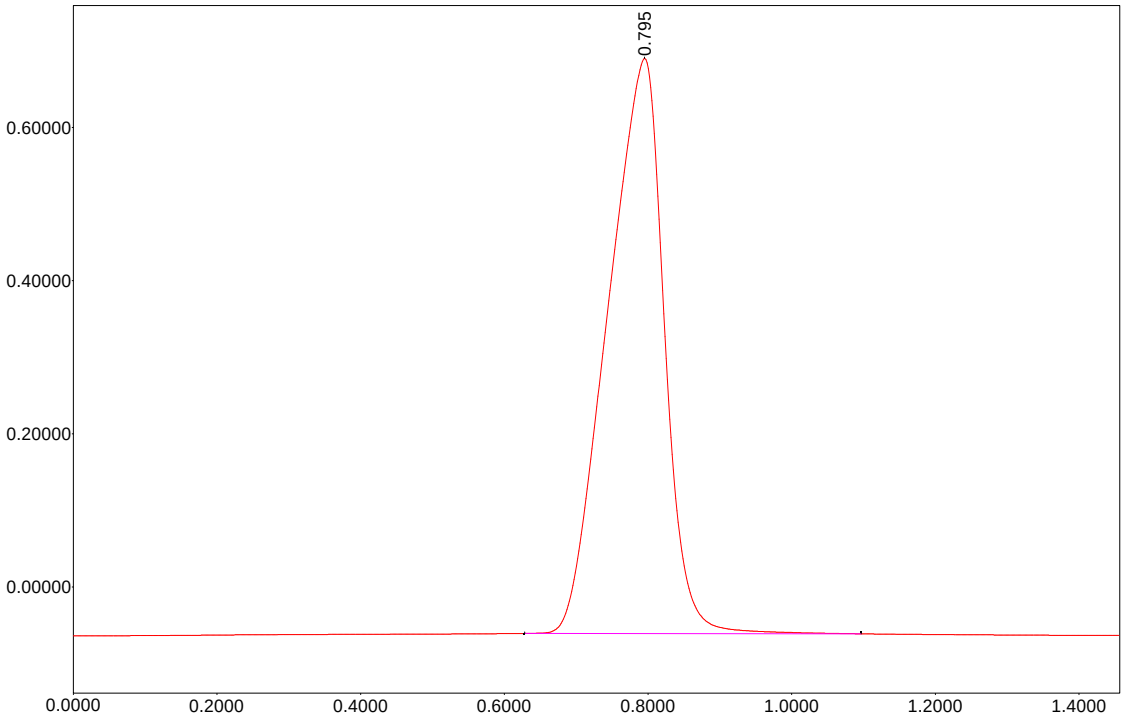
Figure S13. Initial rate of gas evolution (k) vs. temperature (T) in water.



#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.748	713.491	BB	19.000	100.000

Figure S14. GC-TCD profile for the H_2 as reference (Column: Molecular sieve).

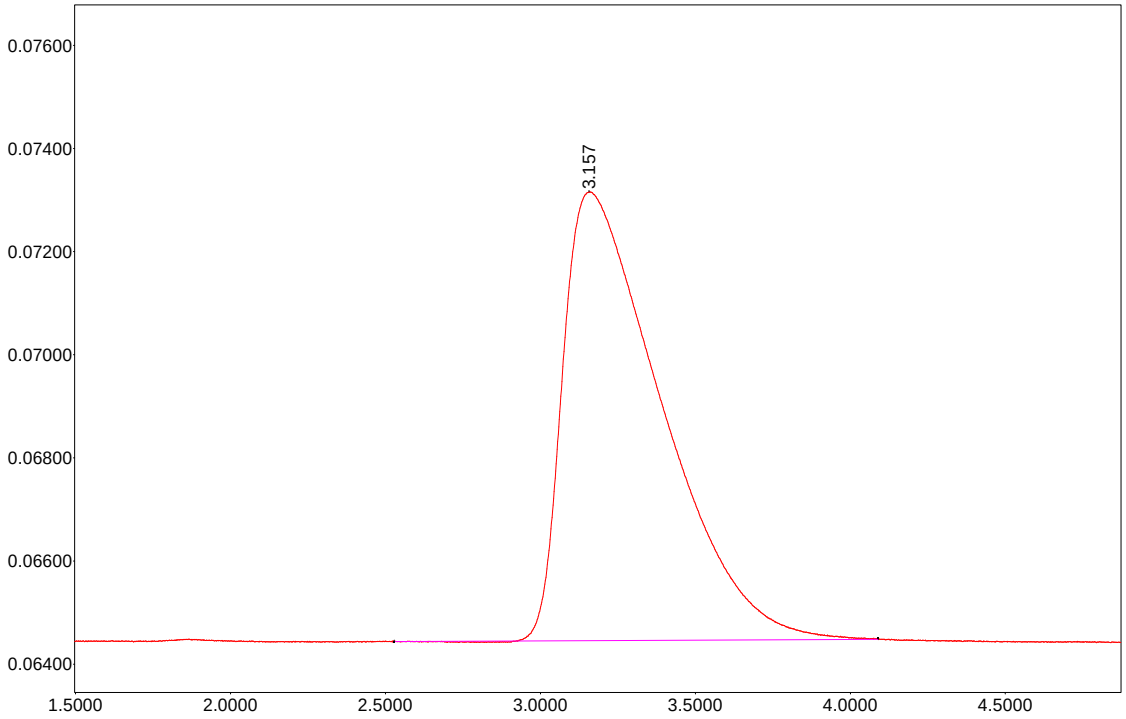
< Chromatogram >



#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.795	4092.157	BB	28.100	100.000

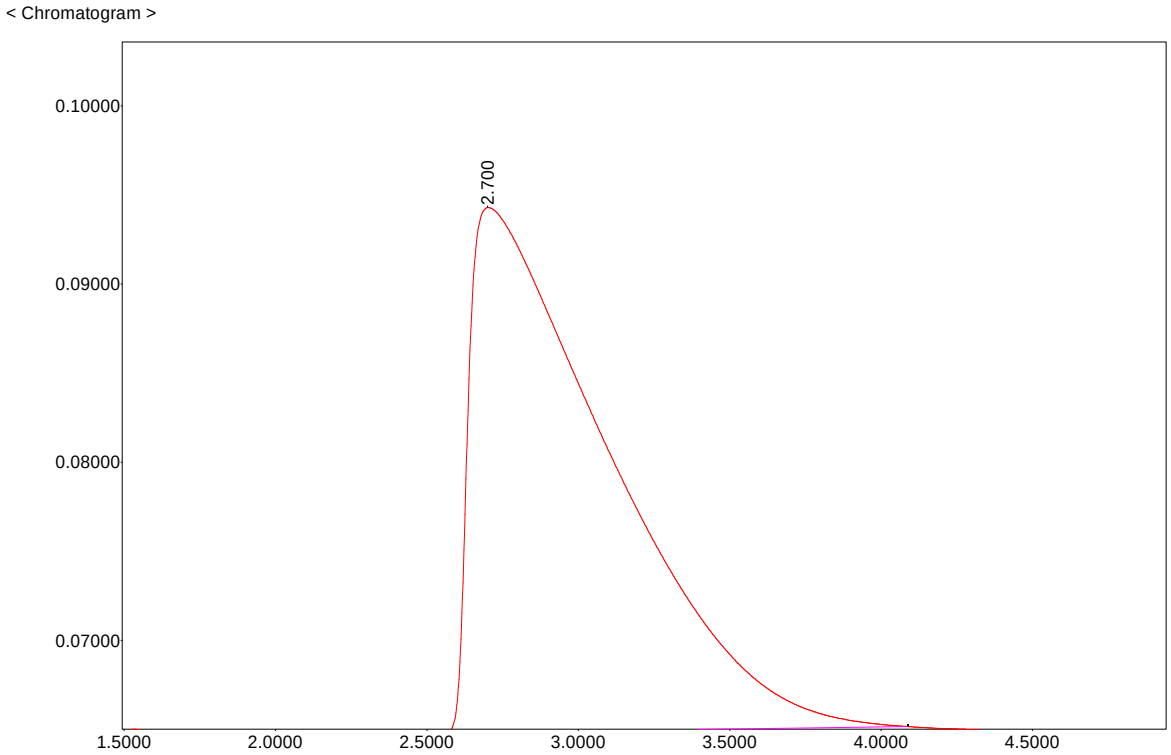
Figure S15. GC-TCD profile for the dehydrogenation using 1.0 mM [Cu(N3Q3)Cl]Cl complex in the presence of 15 mM of formic acid and 15 mM of sodium formate for the H_2 gas evolved in the sample (Column: Molecular sieve).

< Chromatogram >



#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	3.157	192.302	BB	93.700	100.000

Figure S16. GC-TCD profile for the CO_2 as reference (Column: Porapak Q).



#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	2.700	950.013	BB	93.700	100.000

Figure S17. GC-TCD profile for the dehydrogenation using 1.0 mM [Cu(N3Q3)Cl]Cl complex in the presence of 15 mM of formic acid and 15 mM of sodium formate for the CO_2 gas evolved in the sample (Column: Porapak Q).

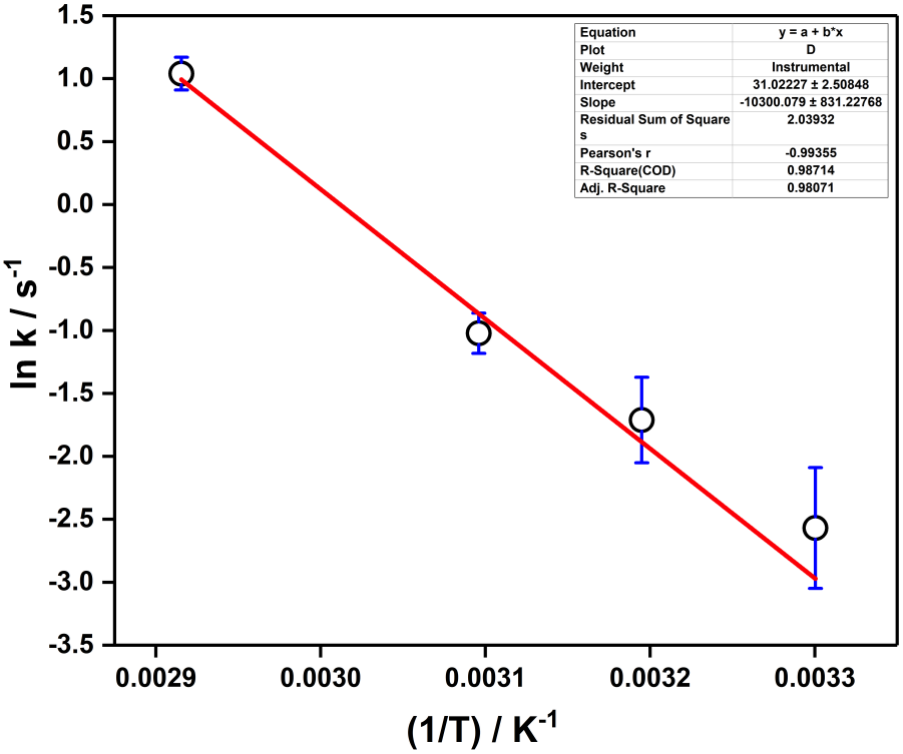


Figure S18. Arrhenius plot for [Cu(N3Q3)Cl]Cl complex to estimate the activation energy.

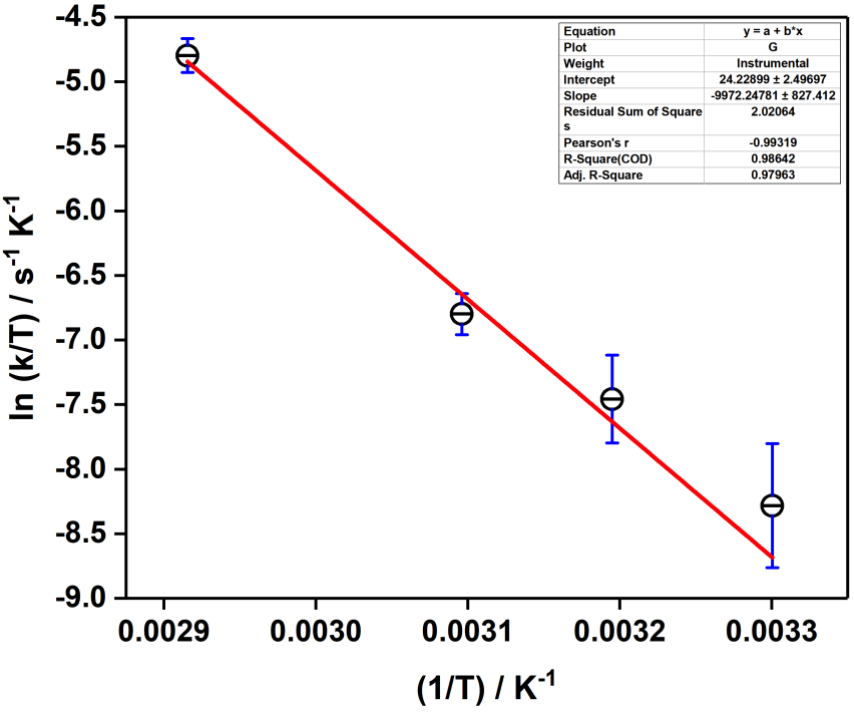


Figure S19. Eyring plot for [Cu(N3Q3)Cl]Cl complex to estimate the $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$.

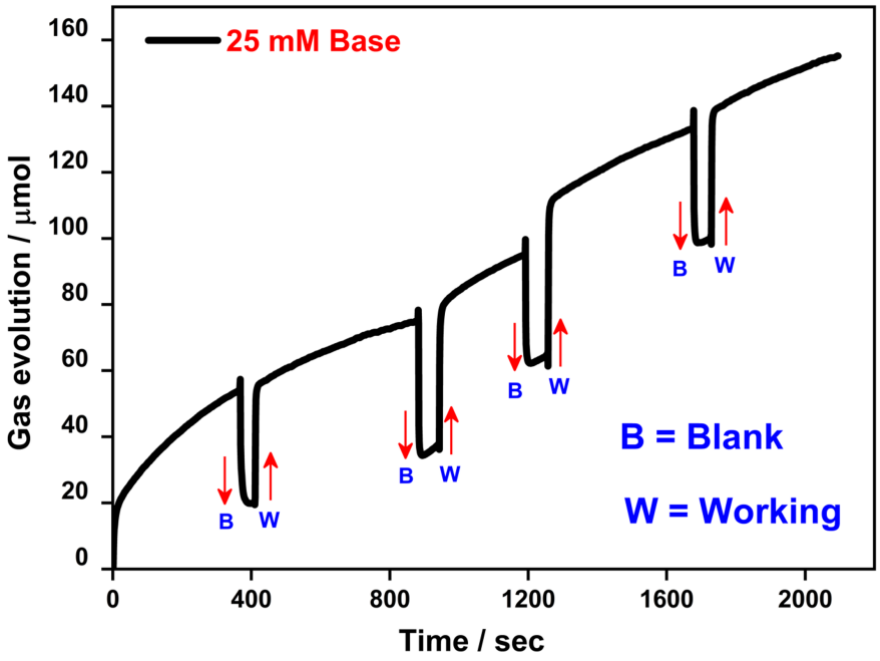


Figure S20. Catalytic cycles for the complex [Cu(N3Q3)Cl]Cl with 25 mM of the base in the presence of 1.0 mM complex and 20 mM acid in water.

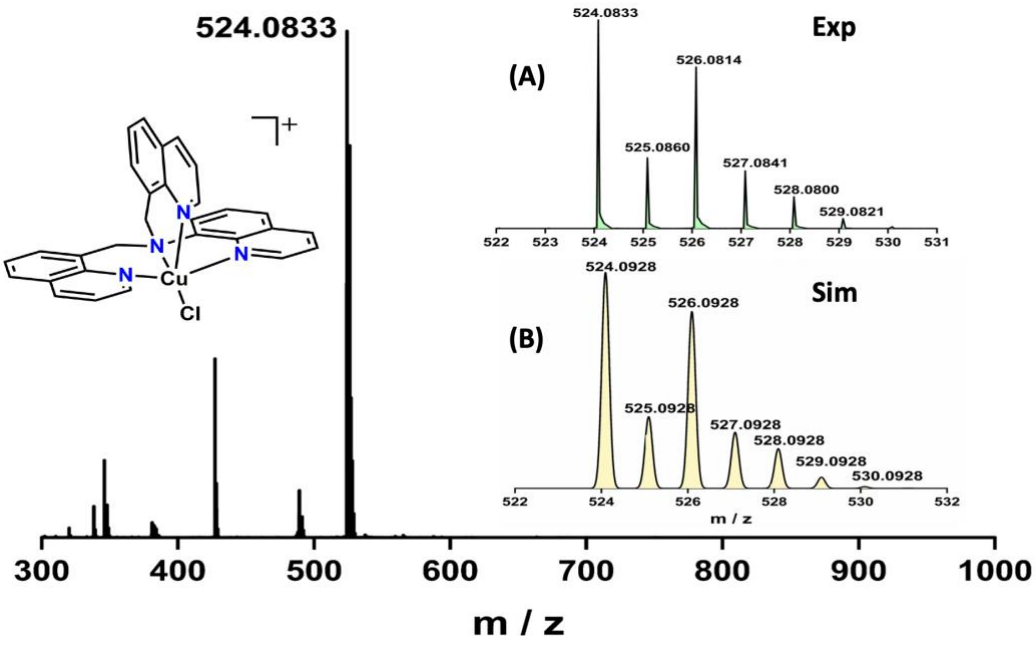


Figure S21. ESI Mass spectra of $[Cu(N3Q3)Cl]^+$ in water.

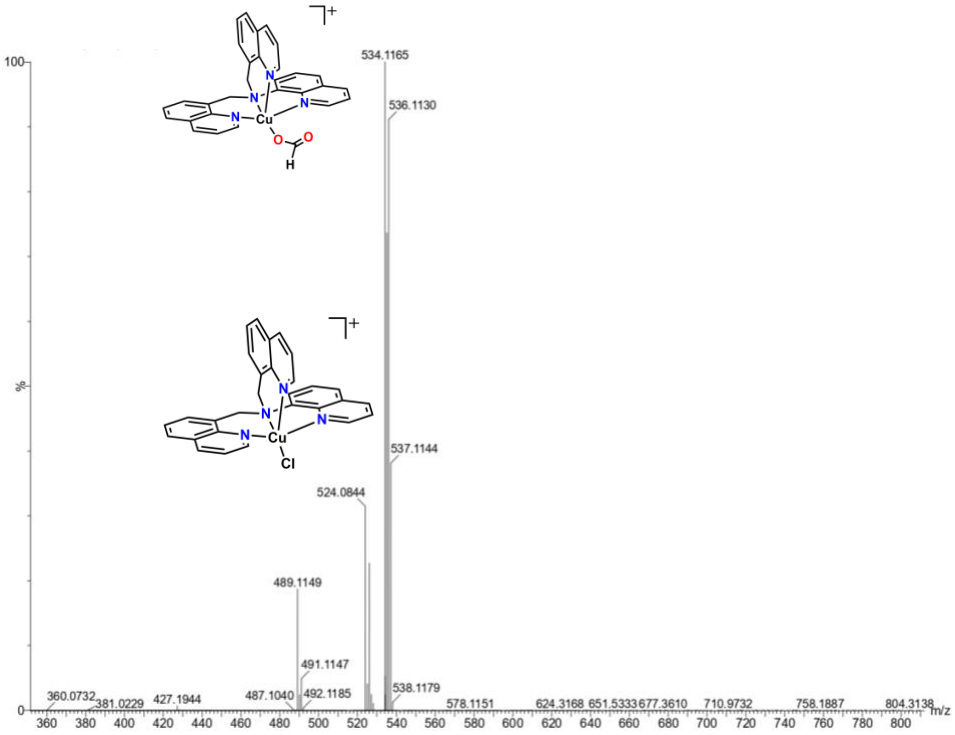


Figure S22. Alteration of colour of the reaction solution and Mass spectra of the reaction aliquots for the base-free catalytic dehydrogenation of formic acid in the presence of 1.0 mM complex and 50 mM acid in water.

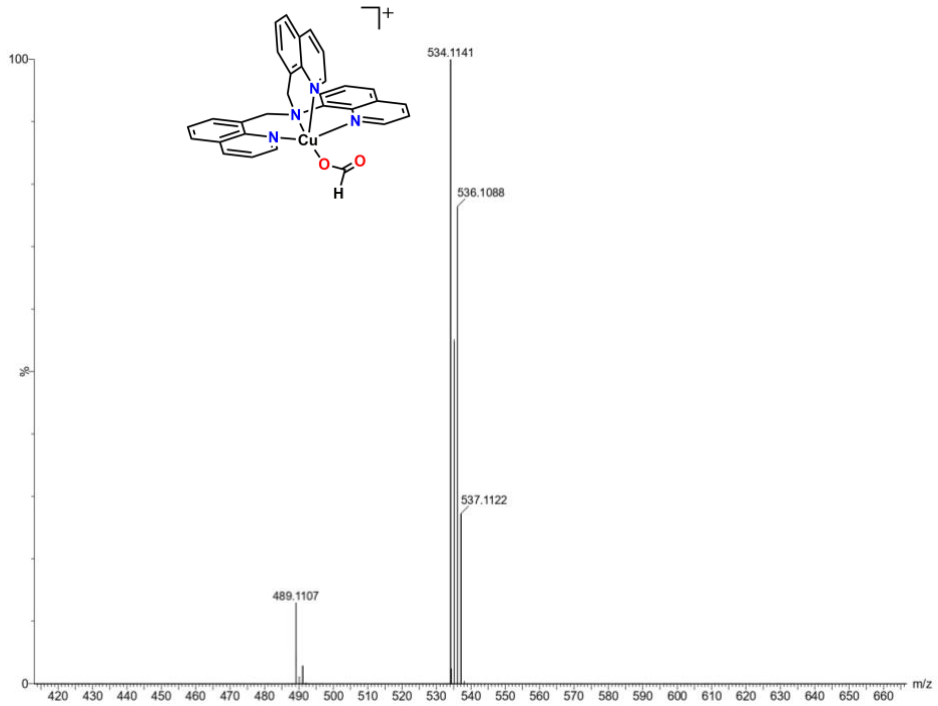


Figure S23. Mass spectra of the reaction aliquots for catalytic dehydrogenation of formic acid in the presence of 1.0 mM complex , 50 mM sodium formate and 50 mM formic acid in water.

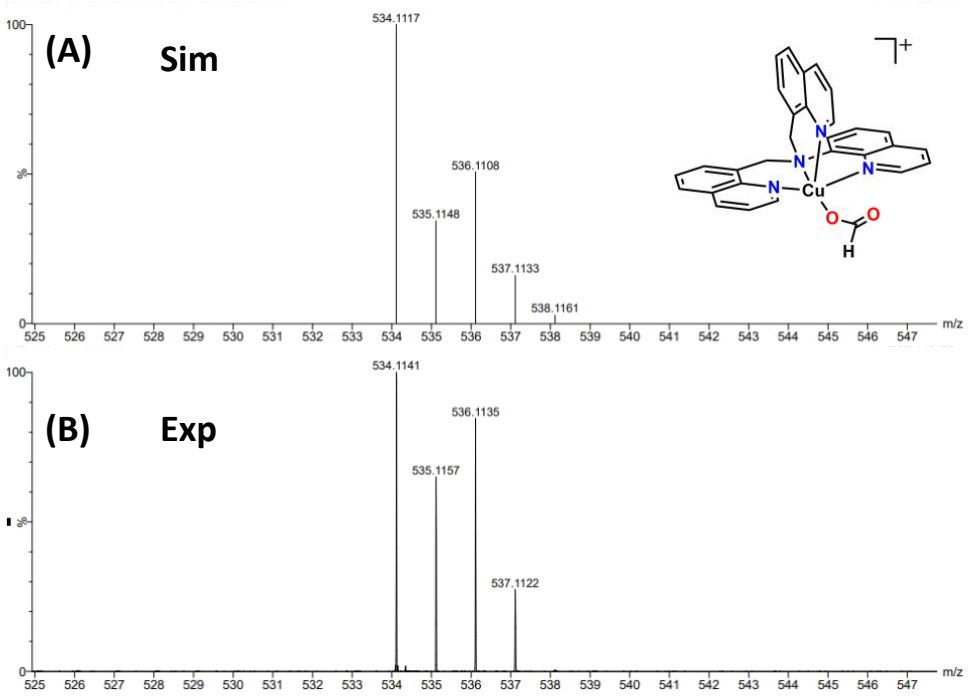


Figure S24. Mass spectra of $[Cu(N3Q3)(HCOO)]^+$ species for the reaction of [Cu(N3Q3)Cl]Cl (1 mM) with formic acid (50 mM) and sodium formate (50mM) in water (1 mL) at 70 °C. ((A) Simulated and (B) Experimental).

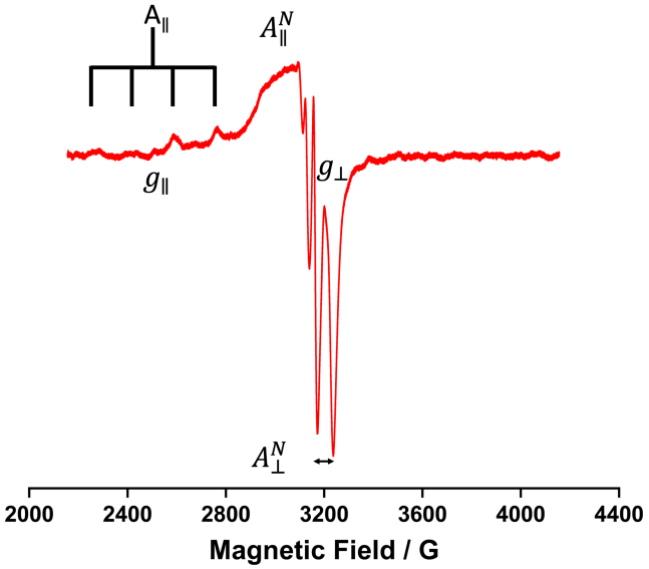


Figure S25. X-band EPR spectra of [Cu(N3Q3)Cl]Cl complex with NaH was recorded at 120 K in water.

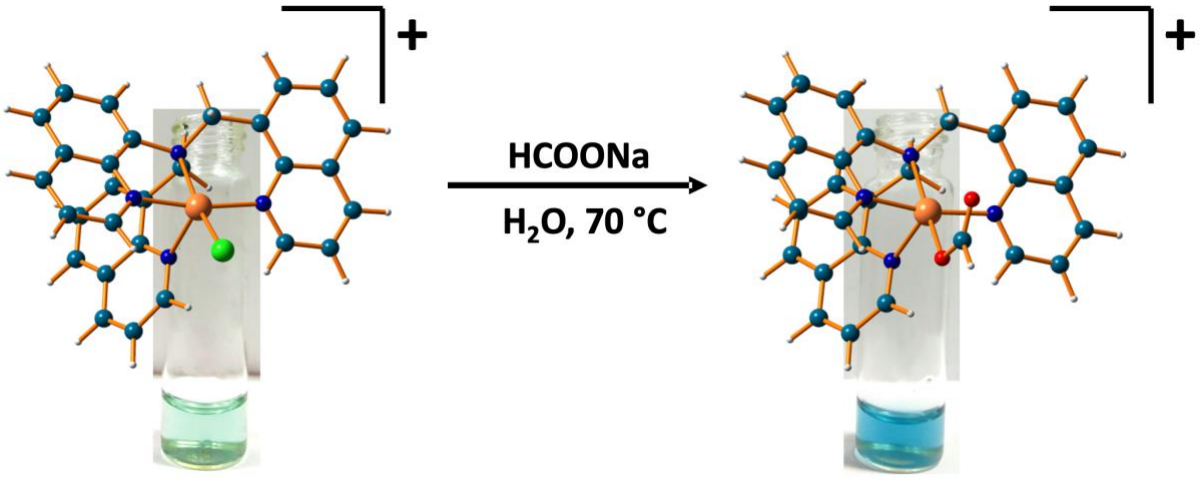


Figure S26. Alteration of the colour with adding HCOONa to a solution of [Cu(N3Q3)Cl]Cl.

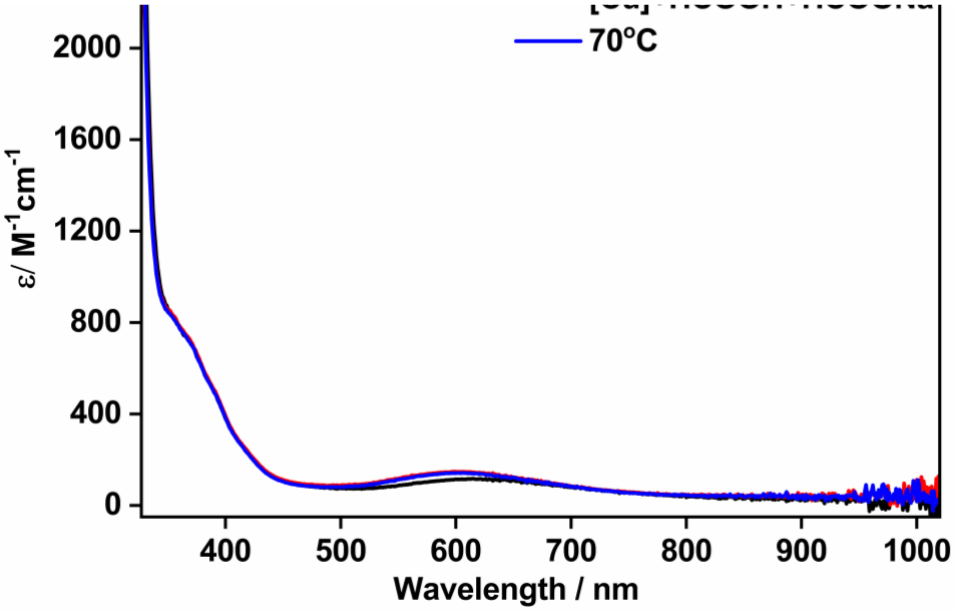


Figure S27. UV-Vis spectra of [Cu] Complex in water medium.

Table S1. Crystal data and structure refinement for [Cu(N3Q3)Cl]Cl.

Identification code	CCDC 2233439
Empirical formula	$C_{29}H_{22}Cl_2CuN_4$
Formula weight	560.96
Temperature/K	298
Crystal system	monoclinic
Space group	C2/c
a/Å	19.874(3)
b/Å	18.630(2)
c/Å	15.830(2)
α/°	90
β/°	115.041(4)
γ/°	90
Volume/Å^3	5310.0(12)
Z	4
ρ_{calc}g/cm^3	1.4033
μ/mm^{-1}	1.049
F(000)	2301.7
Crystal size/mm^3	0.26 × 0.24 × 0.22
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.56 to 49
Index ranges	-26 ≤ h ≤ 26, -24 ≤ k ≤ 24, -21 ≤ l ≤ 21
Reflections collected	42267
Independent reflections	4265 [R_{int} = 0.0447, R_{sigma} = 0.0288]
Data/restraints/parameters	4265/0/330
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0363, wR_2 = 0.0956
Final R indexes [all data]	R_1 = 0.0408, wR_2 = 0.1012
Largest diff. peak/hole / e Å^{-3}	0.84/-1.00

Table S2. Selected bond lengths

Atom	Atom	Length/Å
Cu1	Cl1	2.2873(7)
Cu1	N3	2.050(2)
Cu1	N2	2.045(2)
Cu1	N4	2.249(2)
Cu1	N1	2.022(2)

Table S3. Selected bond angles

Atom	Atom	Atom	Angle/°
N3	Cu1	Cl1	90.92(6)
N2	Cu1	Cl1	160.37(6)
N2	Cu1	N3	90.54(8)
N4	Cu1	Cl1	106.82(6)
N4	Cu1	N3	93.30(8)
N4	Cu1	N2	92.63(8)
N1	Cu1	Cl1	92.00(7)
N1	Cu1	N3	169.90(8)
N1	Cu1	N2	83.50(9)
N1	Cu1	N4	95.11(8)

Table S4. Calculation for Eyring plot for [Cu(N3Q3)Cl]Cl complex.

Temperature / ℃	Slop (k)	k/T	ln(k)	ln(k/T)	1/T
30	0.08794	0.00029	-2.43	-8.145	0.0033
40	0.14226	0.00045	-1.950	-7.706	0.0031
50	0.15932	0.00049	-1.836	-7.621	0.0030
70	0.27604	0.00080	-1.287	-7.130	0.0029

Table S5. Distance (Å) between atoms present in the optimized geometry of intermediates and TS.

Bonds	**[Cu]**	**[Cu]-A**	**[Cu]-B**	**TS1**	**[Cu]-C**	**TS2**
Cu-Cl	2.34	2.12	2.0	1.92	1.57	1.79
Cu-N1	2.07	2.02	2.06	1.99	2.11	2.03
Cu-N2	2.1	2.07	2.09	2.09	2.15	2.08
Cu-N3	2.04	2.0	2.03	1.98	2.06	2.01
Cu-N4	2.32	2.27	2.32	2.23	2.36	2.29

Table S6. Angles between atoms present in N-Cu-X; X = Cl, H_2O, $HCOO^-$ and H^-.

Angle	**[Cu] X = Cl**	**[Cu]-A X = H_2O**	**[Cu]-B X = $HCOO^-$**	**TS1**	**[Cu]-C X = H^-**	**TS2**
N2-Cu-X	163.85	154.67	170.8	140.05	170.1	159.65
N4-Cu-X	106.22	114.48	98.15	125.01	101.1	108.01

Table S7. Cu 3d-orbital occupancy and energy of the complexes

	Orbitals	**Energy (in Hartree)**
[Cu]-B	dxy	-0.38148
	dxz	-0.33993
	dyz	-0.35479
	dx^2-y^2	-0.25586
	dz^2	-0.35568
[Cu]-C	dxy	-0.33022
	dxz	-0.33333
	dyz	-0.28858
	dx^2-y^2	-0.28882
	dz^2	-0.29978

Table S8. The relative single point energies for optimized [Cu]. The energies are reported in kcal/mol and are in relative to 6-311+G(2df,p) basis set.

Basis Set	**Single point energy (kcal/mol)**
6-311+G(2df,p)	0
6-311+G(d)	69.6
6-311+G(d,p)	48.0
6-311+G(2d,p)	25.9
6-311+G(df,p)	16.6

Table S9. The relative single point energies for optimized [Cu]. The energies are reported in kcal/mol and are in relative to B3LYP-D3 functional.

Functional	**Single point energy (kcal/mol)**
B3LYP	54.6
B3LYP-D3	0
B3LYP-D3BJ [15]	-56.9

Cartesian coordinates, imaginary vibrational modes for transition states, and Gibbs free energies for the key structures involved in this study.

[Cu(N3Q3)Cl]Cl optimized structure:

[Cu]

Cu	-0.38504300	0.53775200	1.01927900
Cl	-0.72828900	2.12393700	2.70563400
N	-2.32909100	0.69103600	0.33925400
N	-0.18899400	-1.25593100	-0.04917100
N	0.60050300	1.67056400	-0.74297100
N	1.47947600	0.03111400	1.68914700
C	-3.57244300	-2.71420600	-0.28918600
H	-3.21724500	-3.73844700	-0.28499000
C	-4.93823800	1.24570800	-0.49609900
H	-5.95491800	1.45221200	-0.81060600
C	0.94463400	2.90868800	-0.43295200
H	0.39554800	3.36325600	0.38525600
C	-0.30888600	-0.98385600	-1.52447100
H	-0.49057500	-1.92612700	-2.04744600
H	-1.18653400	-0.35517800	-1.65863600
C	-1.30581200	-2.10602700	0.48223600
H	-1.14658200	-3.13985300	0.16876300
H	-1.21583700	-2.08507300	1.57188500
C	-4.91201500	-2.46409200	-0.65167400
H	-5.56048500	-3.29360000	-0.90497300
C	1.97987400	3.61864900	-1.07266400
H	2.20348000	4.63288200	-0.76835500
C	2.69585800	2.98497000	-2.05706000
H	3.51532300	3.48382800	-2.56256400
C	-3.16390200	-0.35607700	0.02929700
C	0.89768600	-0.30076100	-2.11923200
C	-5.37365100	-1.17441200	-0.70312500
H	-6.39211200	-0.95572300	-1.00219100

C	3.55391800	0.30204800	2.85588800
H	4.14561200	0.91744900	3.52024500
C	-4.50979200	-0.09721300	-0.38506900
C	-2.76337800	1.93612900	0.19812200
H	-2.06079700	2.71850000	0.44524800
C	1.61801200	-0.94294500	-3.10500700
H	1.33734700	-1.94950700	-3.39365300
C	1.27555000	1.02493500	-1.74393400
C	3.07129100	0.95464600	-3.43010500
H	3.89718700	1.44684900	-3.93125000
C	2.36395600	1.65745800	-2.42190000
C	-2.69833500	-1.70278800	0.05915200
C	1.09677600	-1.86053600	0.28395400
C	4.03287700	-0.88541400	2.35886800
H	5.02211400	-1.24210600	2.62183300
C	3.63370600	-2.88840600	0.92207200
H	4.61507500	-3.27839100	1.16500600
C	2.70675300	-0.32605100	-3.76052700
H	3.24359200	-0.87000200	-4.52818400
C	-4.06106100	2.26373200	-0.22357900
H	-4.34280100	3.30395400	-0.31584800
C	1.93544700	-1.14663600	1.16677800
C	3.22488400	-1.65595600	1.48783100
C	1.51914600	-3.05707200	-0.24677600
H	0.88420000	-3.60875800	-0.92876500
C	2.25942800	0.72744700	2.49746800
H	1.84227900	1.64942400	2.87950500
C	2.79357900	-3.57350900	0.07643100
H	3.10483500	-4.51552500	-0.35737300

[Cu]-A

Cu	0.38616700	0.31431800	-1.10977500

N	2.31572400	0.63017900	-0.62250800
N	0.21333900	-1.23638400	0.25002400
N	-0.49295900	1.84064200	0.32237600
N	-1.47897700	-0.20780700	-1.62777800
C	3.62970600	-2.47388900	0.85194700
H	3.29942700	-3.47242200	1.11399700
C	4.92173600	1.41915000	-0.02382400
H	5.93772800	1.71676000	0.20832300
C	-0.76725800	3.02231000	-0.20665000
H	-0.17382400	3.31605400	-1.06611600
C	0.28842600	-0.65454400	1.63682900
H	0.42663500	-1.46970600	2.35109100
H	1.17932500	-0.02960200	1.66784700
C	1.35844700	-2.15051400	-0.06608300
H	1.22909300	-3.08757600	0.47863300
H	1.27870200	-2.38199200	-1.13137800
C	4.96285400	-2.10792600	1.13141700
H	5.62795600	-2.82807000	1.59125500
C	-1.78882400	3.87296700	0.25491400
H	-1.95173800	4.82737900	-0.22789600
C	-2.57173200	3.44434600	1.29721400
H	-3.38769200	4.05329600	1.66995500
C	3.16985100	-0.29096500	-0.06469600
C	-0.92197100	0.15971500	2.02179100
C	5.39981200	-0.84379500	0.83381800
H	6.41557400	-0.53601400	1.05206000
C	-3.58106400	-0.06399800	-2.76202800
H	-4.19174800	0.47125100	-3.47614300
C	4.51360200	0.09340200	0.24667400
C	2.73189200	1.87265100	-0.83977700
H	2.00943900	2.56221700	-1.25748600
C	-1.71627100	-0.27375800	3.06349200

H	-1.48975800	-1.22029800	3.54044800
C	-1.22939400	1.40654200	1.39516100
C	-3.09790500	1.69969200	2.97497200
H	-3.92144200	2.30285000	3.33968700
C	-2.31515700	2.18851000	1.89854000
C	2.73290900	-1.61002600	0.25452500
C	-1.06564500	-1.89864900	0.00729800
C	-4.04226500	-1.18741200	-2.11723800
H	-5.03688800	-1.57093000	-2.31254800
C	-3.61010200	-3.00040600	-0.45184600
H	-4.59391900	-3.41940800	-0.62570100
C	-2.80864400	0.48371300	3.53979900
H	-3.40501000	0.10177500	4.35922200
C	4.03096900	2.31486600	-0.56045200
H	4.30095700	3.34104700	-0.76813400
C	-1.92012700	-1.31015900	-0.95013500
C	-3.21524200	-1.84983300	-1.17840200
C	-1.47769300	-3.01082900	0.70179700
H	-0.83664400	-3.45924300	1.45081500
C	-2.28129800	0.39880000	-2.48724800
H	-1.89317000	1.28446900	-2.97539400
C	-2.75497600	-3.56748900	0.46312400
H	-3.05760600	-4.44392500	1.02201100
O	0.71968300	1.15124800	-3.02634200
H	1.64008900	1.25807700	-3.30277300
H	0.29049700	0.67758400	-3.75196200

[Cu]-B

Cu	0.38379100	0.81275500	-0.62120400
N	2.34355000	0.69696600	0.01169100
N	0.11748600	-1.23162000	-0.29945300
N	-0.62144400	1.25036900	1.41986400

N	-1.44213900	0.65739600	-1.49814100
C	3.43300300	-2.79750700	-0.33978500
H	3.04813300	-3.75390600	-0.67490900
C	4.93030400	0.86583500	1.05678800
H	5.93502300	0.92341700	1.45984500
C	-0.90852600	2.53053100	1.58304000
H	-0.29343800	3.22888500	1.02607700
C	0.16349700	-1.52927100	1.17525600
H	0.30349400	-2.60354000	1.31893000
H	1.04439800	-1.02331300	1.56701400
C	1.25759400	-1.85843800	-1.05026600
H	1.07071300	-2.92858400	-1.15855500
H	1.23857100	-1.42348400	-2.05346700
C	4.74981000	-2.73534500	0.16250900
H	5.35004000	-3.63598800	0.19948600
C	-1.96644700	2.99879900	2.38820100
H	-2.14233100	4.06289100	2.47845900
C	-2.76438600	2.07903500	3.02174800
H	-3.60236500	2.39294300	3.63435400
C	3.12455400	-0.43278800	0.03786100
C	-1.06130500	-1.07237800	1.92756100
C	5.25334500	-1.54114100	0.60878400
H	6.25867100	-1.47179800	1.00769800
C	-3.43396000	1.42003000	-2.58088900
H	-3.97925700	2.25866000	-2.99264800
C	4.45264300	-0.37223600	0.56790700
C	2.82534600	1.83638500	0.49029200
H	2.16444800	2.69023700	0.43808100
C	-1.86042800	-2.00396700	2.55691400
H	-1.62500900	-3.05734900	2.45640300
C	-1.38025200	0.31279800	2.06567600
C	-3.28419300	-0.29985300	3.50237900

H	-4.12922600	0.00556700	4.10910600
C	-2.49397000	0.69651800	2.87497900
C	2.62014400	-1.68424900	-0.42350100
C	-1.15498700	-1.63118900	-0.89503700
C	-3.95394300	0.14787400	-2.59609900
H	-4.92938400	-0.04954400	-3.02564200
C	-3.66341400	-2.26372900	-2.00162300
H	-4.63163200	-2.50507800	-2.42407900
C	-2.97450500	-1.62679000	3.33994400
H	-3.57516700	-2.39309000	3.81472500
C	4.11697400	1.96952700	1.02350300
H	4.44207900	2.93190000	1.39533200
C	-1.93739800	-0.61389500	-1.48581100
C	-3.21023900	-0.92217500	-2.04044600
C	-1.62168700	-2.92450000	-0.87303600
H	-1.03566700	-3.71207200	-0.41592900
C	-2.16004800	1.63565100	-2.01831900
H	-1.71166300	2.62006000	-1.98682200
C	-2.88090100	-3.24044100	-1.43184700
H	-3.22686900	-4.26601700	-1.39987500
O	0.60233000	2.69782300	-1.23902800
C	1.13845200	2.78531800	-2.40679100
H	1.27293000	3.82639200	-2.75416200
O	1.48653700	1.84351100	-3.12117200

[Cu]-C

Cu	0.39136900	0.34985100	-1.35576000
N	2.47173700	0.49478600	-1.01970500
N	0.20712300	-1.10755300	0.22064600
N	-0.42700200	1.94820900	0.17646500
N	-1.51164700	-0.32540100	-1.77131800
C	3.49911700	-2.29533000	1.14113200

H	3.09600900	-3.21465100	1.55054000
C	5.09828000	1.25983100	-0.41739200
H	6.11336500	1.55260700	-0.17362200
C	-0.69787900	3.09045900	-0.42938400
H	-0.07908600	3.32889900	-1.28806700
C	0.33008600	-0.45513900	1.56733400
H	0.50624300	-1.21615200	2.33327600
H	1.21192700	0.18328700	1.52194600
C	1.33704100	-2.05653900	-0.04971900
H	1.17896600	-2.98487800	0.50414000
H	1.28891800	-2.30169400	-1.11452100
C	4.82003400	-1.92630300	1.47479800
H	5.40240000	-2.56166800	2.13078200
C	-1.73904900	3.95863000	-0.04050600
H	-1.90119900	4.88062500	-0.58397000
C	-2.53773500	3.59302800	1.01454300
H	-3.36285500	4.21946000	1.33542100
C	3.23759300	-0.31527200	-0.21756700
C	-0.87242100	0.37091800	1.94669500
C	5.35405000	-0.77050800	0.96704700
H	6.36723800	-0.46929800	1.20722400
C	-3.60742400	-0.37808800	-2.93039200
H	-4.21962100	0.03834600	-3.71936300
C	4.57881800	0.05724500	0.11602600
C	3.00173600	1.61008700	-1.50382300
H	2.35276800	2.19897000	-2.13924600
C	-1.66141000	-0.00576100	3.01328500
H	-1.43081000	-0.92246200	3.54417700
C	-1.18420300	1.57904500	1.25339200
C	-3.06463900	1.94780500	2.79931500
H	-3.89826000	2.56082100	3.12336000
C	-2.28132200	2.37969800	1.69882600

C	2.70690100	-1.53189100	0.30694900
C	-1.07246200	-1.78780400	0.06880700
C	-4.06235800	-1.39897700	-2.13113700
H	-5.05205200	-1.81825000	-2.27206400
C	-3.61485000	-2.96623200	-0.23941600
H	-4.59533400	-3.41318300	-0.35578800
C	-2.76098900	0.77279800	3.44062500
H	-3.35593100	0.43725700	4.28155200
C	4.31347800	2.03436100	-1.23288400
H	4.67425300	2.95895700	-1.66377300
C	-1.94036600	-1.33022800	-0.95332600
C	-3.22981400	-1.91493200	-1.10734200
C	-1.47730600	-2.81453400	0.89073200
H	-0.82506800	-3.17061600	1.67877300
C	-2.30973100	0.13061900	-2.71839100
H	-1.90709200	0.92562800	-3.33411800
C	-2.75064100	-3.40713500	0.73470900
H	-3.04245100	-4.21086100	1.39942800
H	0.47127900	1.20377500	-2.66927800

TS1

Cu	0.39166200	0.68011900	-0.51981000
O	0.60886000	3.84004200	-0.76445100
N	2.31944300	0.59257100	-0.04702400
N	0.11837800	-1.38921300	-0.48349800
N	-0.45380200	1.00134800	1.51360900
N	-1.44347500	0.71677700	-1.26963200
C	3.45776800	-2.86595500	-0.61311300
H	3.08754000	-3.80925500	-0.99764700
C	4.92395000	0.74878300	0.92868500
H	5.93723000	0.79896500	1.31034900
C	-0.63255200	2.26764400	1.85931700

H	0.00449600	2.99283100	1.36612100
C	0.13628100	-1.81976200	0.95491700
H	0.19489700	-2.91060900	0.99897500
H	1.05302700	-1.42106400	1.38879100
C	1.26330300	-1.93849700	-1.27236900
H	1.10657000	-3.00497800	-1.44935200
H	1.23427900	-1.43774000	-2.24367500
C	4.77808700	-2.80815800	-0.12119800
H	5.39291300	-3.69935900	-0.13617700
C	-1.62224700	2.69634800	2.76406300
H	-1.70813700	3.74800500	3.00377200
C	-2.47716000	1.76167000	3.29053000
H	-3.27415000	2.05056300	3.96652500
C	3.10987400	-0.53235100	-0.10559100
C	-1.05230500	-1.34376900	1.75364200
C	5.26815800	-1.62873100	0.37457300
H	6.27846400	-1.55970700	0.76020900
C	-3.48211800	1.67933300	-2.06673800
H	-4.04182600	2.58265200	-2.26741300
C	4.44805300	-0.47302900	0.40027500
C	2.79990000	1.72226500	0.46274900
H	2.13032700	2.57403800	0.46704200
C	-1.92191600	-2.27963900	2.27590400
H	-1.76934600	-3.32718100	2.04272800
C	-1.26065500	0.03587000	2.06277300
C	-3.18550700	-0.60507200	3.46196700
H	-3.99054300	-0.31194100	4.12623000
C	-2.32308400	0.39620600	2.94844200
C	2.62203700	-1.76628700	-0.63143500
C	-1.16100300	-1.65674800	-1.12801500
C	-4.00547700	0.43452100	-2.32514300
H	-4.99919900	0.32595700	-2.74382700

C	-3.71046600	-2.04534500	-2.24838900
H	-4.69622500	-2.19238500	-2.67319400
C	-2.99479600	-1.91972400	3.12004000
H	-3.65249000	-2.68970300	3.50426000
C	4.10407300	1.84839900	0.95855400
H	4.43174300	2.79926400	1.35587900
C	-1.94775600	-0.53732400	-1.48410600
C	-3.24510700	-0.72399900	-2.03472300
C	-1.64235000	-2.92634300	-1.34238800
H	-1.05317000	-3.78917000	-1.05788000
C	-2.18387900	1.78073700	-1.53487800
H	-1.73973100	2.74456900	-1.31975900
C	-2.92088200	-3.11963400	-1.91356600
H	-3.27770200	-4.12931500	-2.07326500
C	0.78389200	3.24493600	-1.84152600
O	0.86070400	3.61671700	-3.01417600
H	0.89580800	2.07960000	-1.73887900

TS2

Cu	0.31798900	-0.19300600	-0.94628300
N	2.16508200	0.56374000	-0.57755600
N	-0.03164100	-0.57337200	1.06749700
N	-0.86300600	1.76212200	-0.84492200
N	-1.38863600	-1.21726100	-1.21331100
C	3.25695700	-0.73703400	2.68480200
H	2.90425400	-1.38514700	3.47882800
C	4.64515500	1.81792900	-0.34081500
H	5.60897900	2.30340600	-0.23902000
C	-1.10909900	2.31037200	-2.02368700
H	-0.39474000	2.09732400	-2.81191700
C	-0.18061700	0.73311500	1.79502200
H	-0.11007200	0.55503300	2.87081800

H	0.66730300	1.35143600	1.50370100
C	1.18094800	-1.35023100	1.48753000
H	0.99736800	-1.80266800	2.46403800
H	1.29148800	-2.15842700	0.75859300
C	4.51690200	-0.11851500	2.82541600
H	5.10409700	-0.30119000	3.71682000
C	-2.23446900	3.10989300	-2.30023400
H	-2.36710100	3.52658300	-3.28998000
C	-3.14916600	3.31728300	-1.29843200
H	-4.04238200	3.90738800	-1.47074700
C	2.92679400	0.31264400	0.53695200
C	-1.46877300	1.45312600	1.48267100
C	4.98385400	0.71003700	1.83861900
H	5.94692400	1.19907900	1.92660400
C	-3.21564200	-2.17916600	-2.41956900
H	-3.68364000	-2.34239500	-3.38089700
C	4.20016500	0.94937200	0.68232600
C	2.61948600	1.38183500	-1.51618200
H	1.98293100	1.53048200	-2.37852600
C	-2.38675100	1.66164400	2.49112100
H	-2.18886100	1.25684600	3.47703300
C	-1.73828300	1.98788700	0.18562600
C	-3.83787000	2.94284000	1.05277200
H	-4.73772000	3.52232200	0.88028500
C	-2.92643700	2.75666800	-0.01746300
C	2.46218900	-0.55439500	1.57023400
C	-1.23313900	-1.39665000	1.16250100
C	-3.76739200	-2.66647300	-1.25848300
H	-4.69200900	-3.23174600	-1.27759600
C	-3.61346100	-2.89415500	1.22682700
H	-4.53293000	-3.46681100	1.25046100
C	-3.57451900	2.39720500	2.28353000

H	-4.26720800	2.53316000	3.10508300
C	3.85678800	2.03710200	-1.44145800
H	4.16149600	2.69336400	-2.24521500
C	-1.91587400	-1.68074100	-0.04152000
C	-3.12362100	-2.43058700	-0.01917700
C	-1.73106700	-1.86368800	2.35578800
H	-1.21966300	-1.64762200	3.28558600
C	-2.00980100	-1.45512800	-2.35494000
H	-1.54115100	-1.06374700	-3.24926200
C	-2.92640200	-2.61780800	2.38531700
H	-3.29997500	-2.97220800	3.33783400
H	0.76768800	-0.47855400	-2.65028300
O	1.80551000	-2.40499900	-1.77790000
H	1.19569100	-1.21930400	-2.40645100
C	3.08933400	-2.38365300	-1.80053800
H	3.56236200	-3.06963500	-1.06633900
O	3.80892300	-1.69384600	-2.52916700

CO_2

C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.16072300
O	0.00000000	0.00000000	-1.16072300

H_2

H	0.00000000	0.00000000	0.37228800
H	0.00000000	0.00000000	-0.37228800

HCOOH

C	-0.12520300	0.36786100	0.00002600
H	-0.03801200	1.46519900	0.00005300
O	1.04596000	-0.28112700	0.00003600
H	1.78435900	0.34473900	-0.00029100

O -1.17035100 -0.22101100 -0.00002600

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