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Supporting Information

A phenoxo-bridged dicopper(II) complex as a model for phosphatase activity: mechanistic insights from combined experimental and computational Study†

Suman K. Barman, Totan Mandal, Debasis Koley, Francesc Lloret and Rabindranath Mukherjee*

Figues and Tables

Fig. S1. Perspective view of $[Cu^{II}_2(L^1)(\mu\text{-}O_2CMe)_2][NO_3] \cdot 3Et_2O$ (**1** · $3Et_2O$).

Fig. S2. UV-VIS spectrum of **1**.

Fig. S3. Titration-curve obtained for **1** in 33% (v/v) MeOH-H_2O with 0.07 N NaOH.

Fig. S4. Species-distribution curves of **1** in 33% (v/v) MeOH-H_2O as a function of pH.

Fig. S5. ESI-MS spectrum of **1** in MeOH–H_2O (33%) at pH 8.50.

Fig. S6. Simulated (green line) and experimental mass isotopic distribution (red line) for $[Cu^{II}_2(L^1)(HCO_2)_2]^+$, $[Cu^{II}_2(L^1)(HCO_2)(OH)(H_2O)]^+$ and $[Cu^{II}_2(L^1)(H_2O)_4]^+$.

Fig. S7. ^{31}P NMR spectra of the product of HPNP hydrolysis by **1** at different time-intervals in MeOH–H_2O at 30°C (ref. 85% H_3PO_4 as external standard). [Complex] = 4.62×10^{-5} M; [HPNP] = 2.30×10^{-3} M; [buffers] = 20×10^{-3} M; I = 0.1 M ($NaNO_3$), pH = 8.50.

Fig. S8. Time-course for the change in the absorbance for the hydrolysis of HPNP catalysed by **1**. Conditions: [HPNP] = 5×10^{-5} M; [complex] = 30×10^{-5} to 75×10^{-5} M; buffer CHES (pH 8.50), I = 0.1 M ($NaNO_3$) in MeOH–H_2O (33%, v/v) at 30 °C.

Fig. S9. Fitting of raw-data to *pseudo*-first-order mechanism for the hydrolysis of HPNP catalyzed by **1**. Conditions: [HPNP] = 5×10^{-5} M; [complex] = 30×10^{-5} to 75×10^{-5} M; buffer CHES (pH 8.50), I = 0.1 M ($NaNO_3$) in MeOH–H_2O (33%, v/v) at 30 °C.

$[Cu^{II}_2(L^1)(\mu\text{-OMe})(OMe)(HPNP)]^{\#}$.

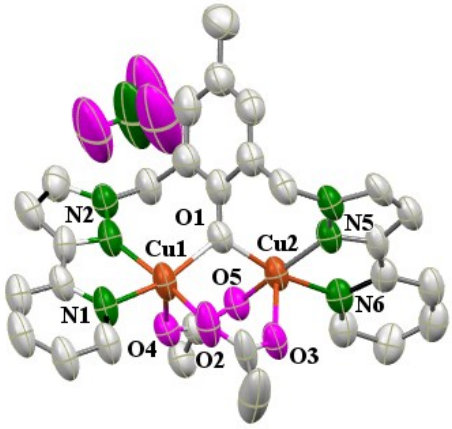


Fig. S1. Perspective view of $[Cu^{II}_2(L^1)(\mu\text{-}O_2CMe)_2][NO_3] \cdot 3Et_2O$ (**1** $\cdot 3Et_2O$), without solvent of crystallization. Selected bond-lengths: Cu1–N1 = 2.057 Å, Cu1–N2 = 1.953 Å, Cu1–O1 = 1.988 Å, Cu1–O2 = 1.920 Å, Cu1–O4 = 2.193 Å, Cu2–N6 = 2.033 Å, Cu2–N5 = 1.965 Å, Cu2–O5 = 1.913 Å, Cu2–O3 = 2.176 Å. These bond-lengths are consistent with that observed for $[Cu^{II}_2(L^1)(\mu\text{-}O_2CMe)_2][ClO_4] \cdot 1.375MeCN \cdot 0.25H_2O$.

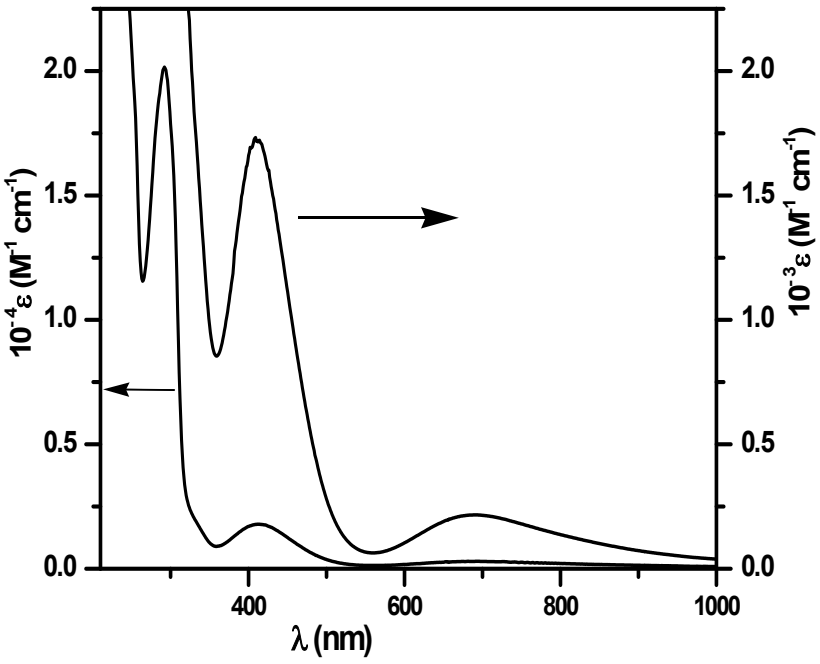


Fig. S2. UV-VIS spectrum of **1** in MeOH.

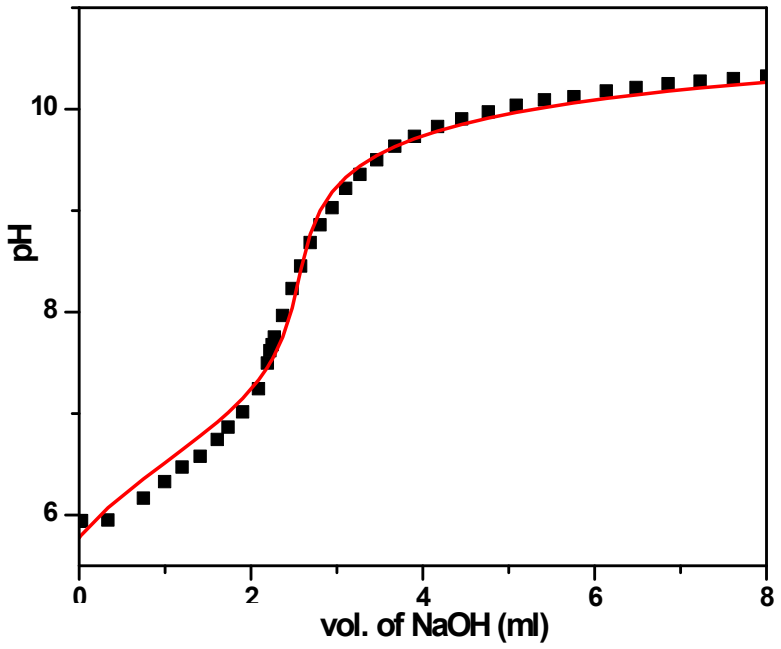


Fig. S3. Titration-curve obtained for **1** in 33% (v/v) MeOH-H_2O with 0.07 N NaOH.

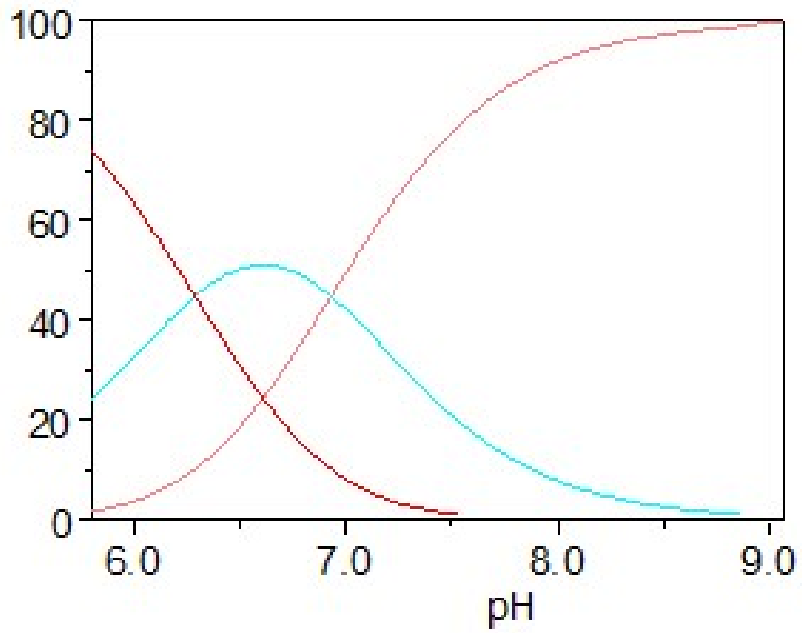


Fig. S4. Species-distribution curves of **1** in 33% (v/v) MeOH-H_2O as a function of pH.

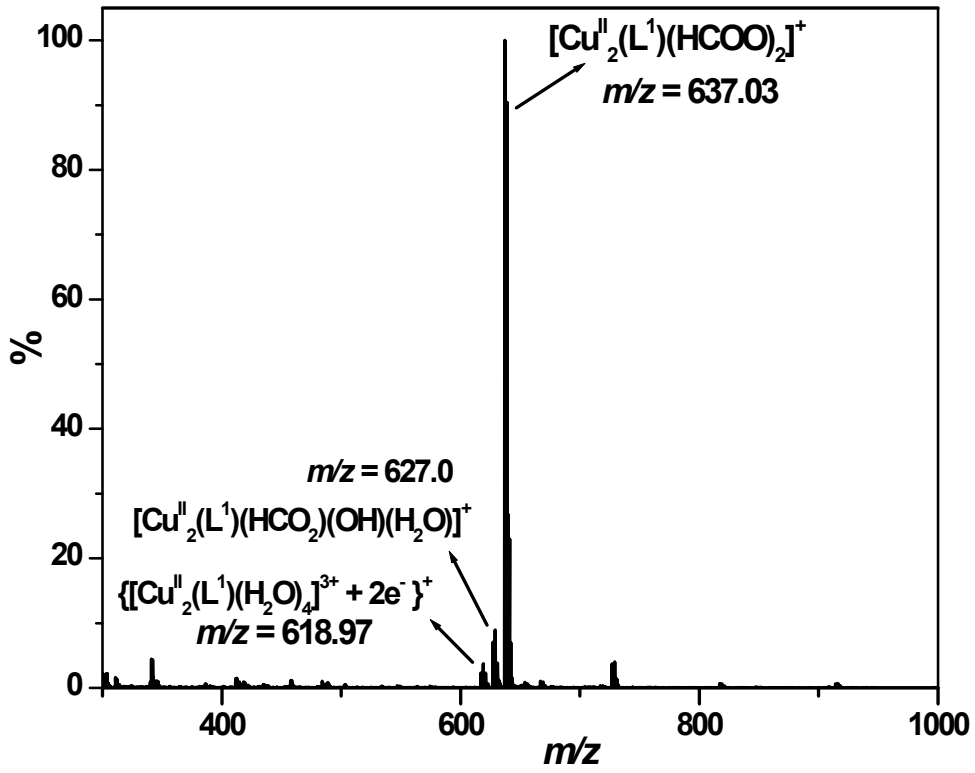


Figure S5. ESI–MS spectrum of **1** in MeOH–H_2O (33%) at pH 8.50.

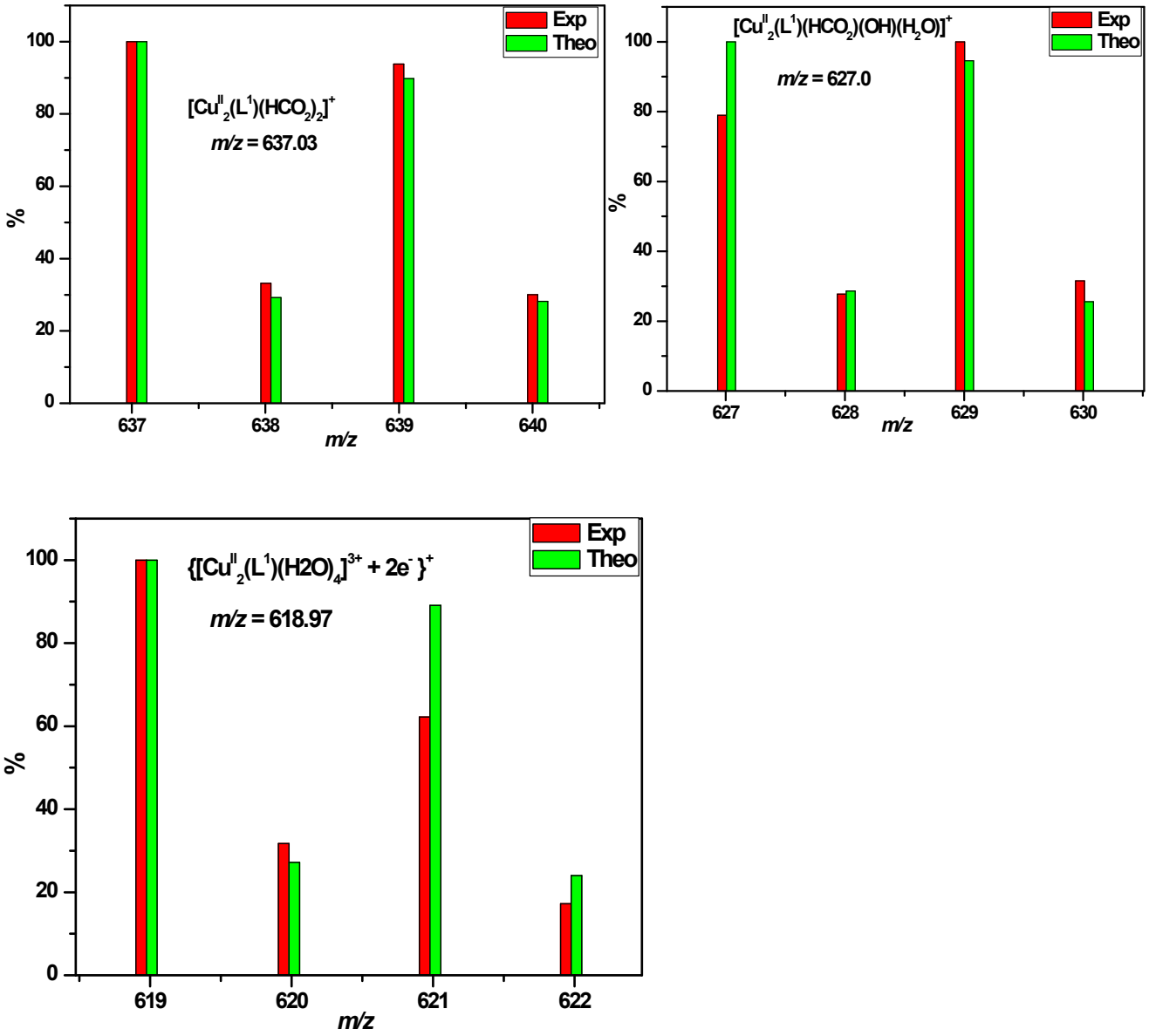


Fig. S6. Simulated (green line) and experimental mass isotopic distribution (red line) for $[Cu^{II}_2(L^1)(HCO_2)_2]^+$, $[Cu^{II}_2(L^1)(HCO_2)(OH)(H_2O)]^+$ and $[Cu^{II}_2(L^1)(H_2O)_4]^+$.

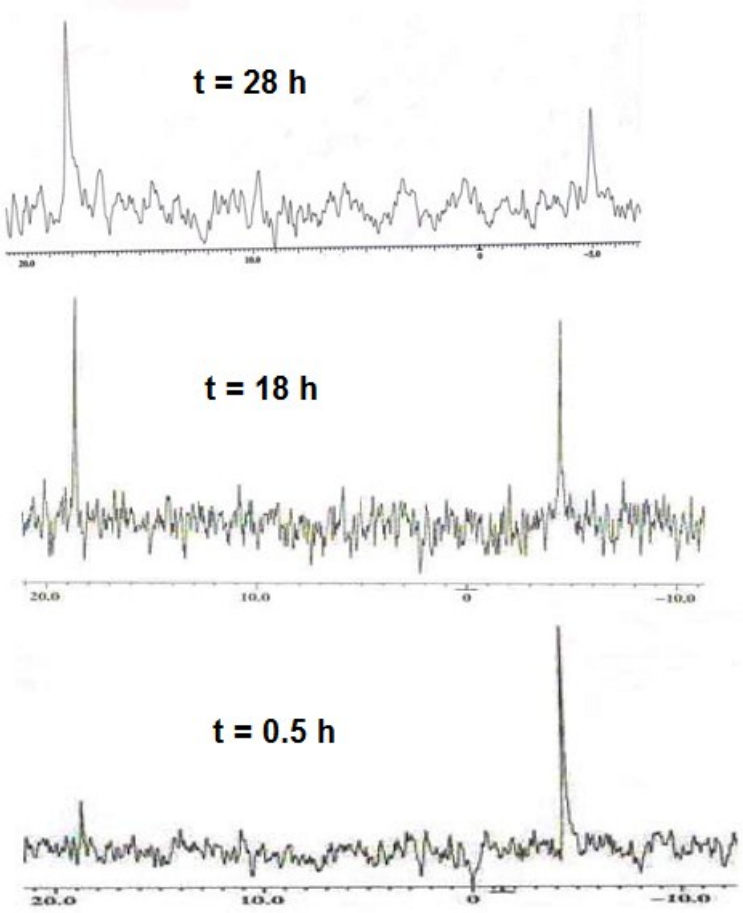


Fig. S7. ^{31}P NMR spectra of the product of HPNP hydrolysis by **1** at different time-intervals in MeOH–H_2O at 30°C (ref. 85% H_3PO_4 as external standard). [Complex] = 4.62×10^{-5} M; [HPNP] = 2.30×10^{-3} M; [buffers] = 20×10^{-3} M; I = 0.1 M ($NaNO_3$), pH = 8.50.

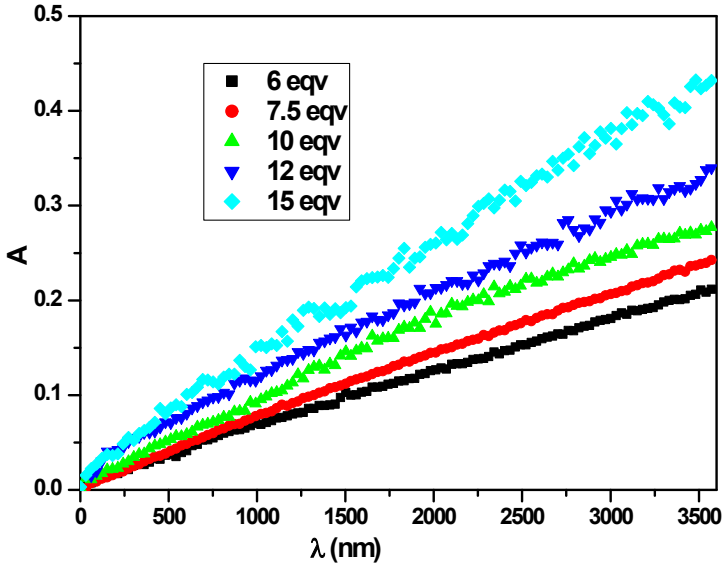
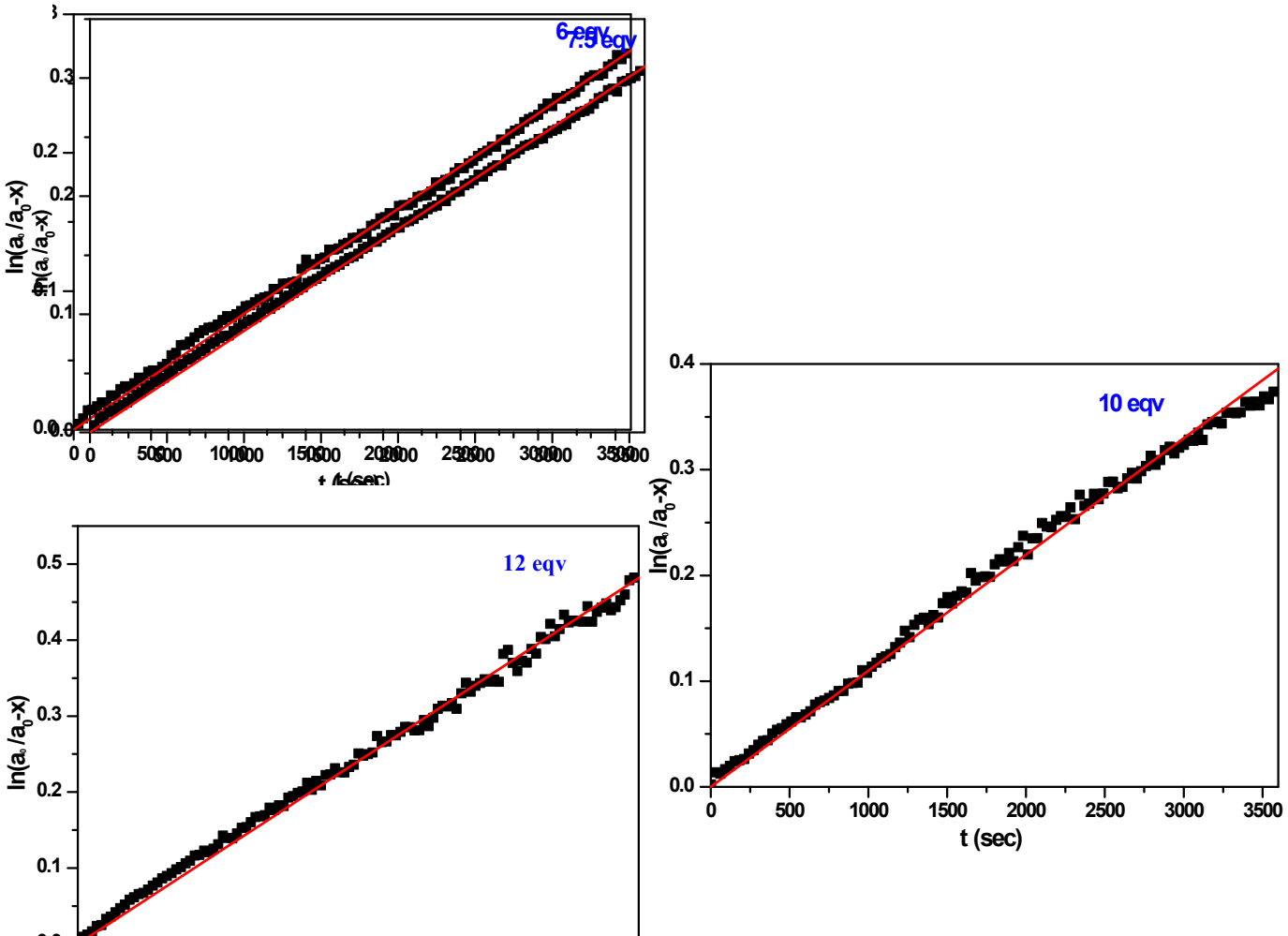


Fig. S8. Time-course for the change in the absorbance for the hydrolysis of HPNP catalysed by **1**. Conditions: [HPNP] = 5×10^{-5} M; [complex] = 30×10^{-5} to 75×10^{-5} M; buffer CHES (pH 8.50), I = 0.1 M ($NaNO_3$) in MeOH–H_2O (33%, v/v) at 30 °C.



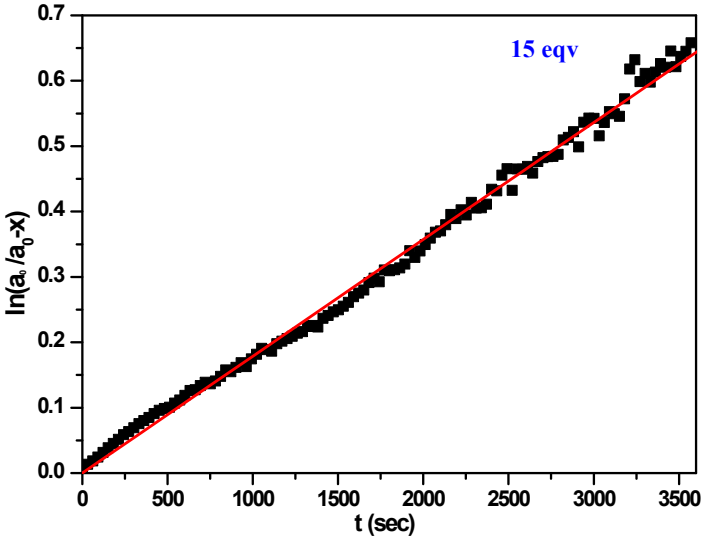


Fig. S9. Fitting of raw-data to *pseudo*-first-order mechanism for the hydrolysis of HPNP catalysed by **1**. Conditions: [HPNP] = 5×10^{-5} M; [complex] = 30×10^{-5} to 75×10^{-5} M; buffer CHES (pH 8.50), I = 0.1 M ($NaNO_3$) in MeOH–H_2O (33%, v/v) at 30 °C.

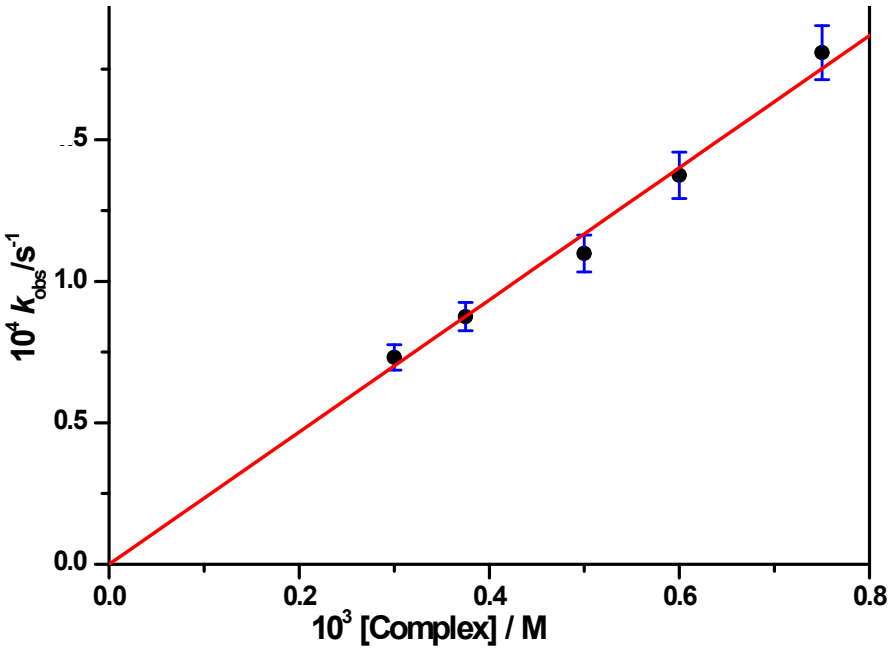


Fig. S10. Dependence of the observed rate-constants on the concentration of **1** for the hydrolysis of HPNP. Conditions: [HPNP] = 5×10^{-5} M; [complex] = 30×10^{-5} to 75×10^{-5} M; buffer CHES (pH 8.50), I = 0.1 M ($NaNO_3$) in MeOH–H_2O (33%, v/v) at 30 °C.

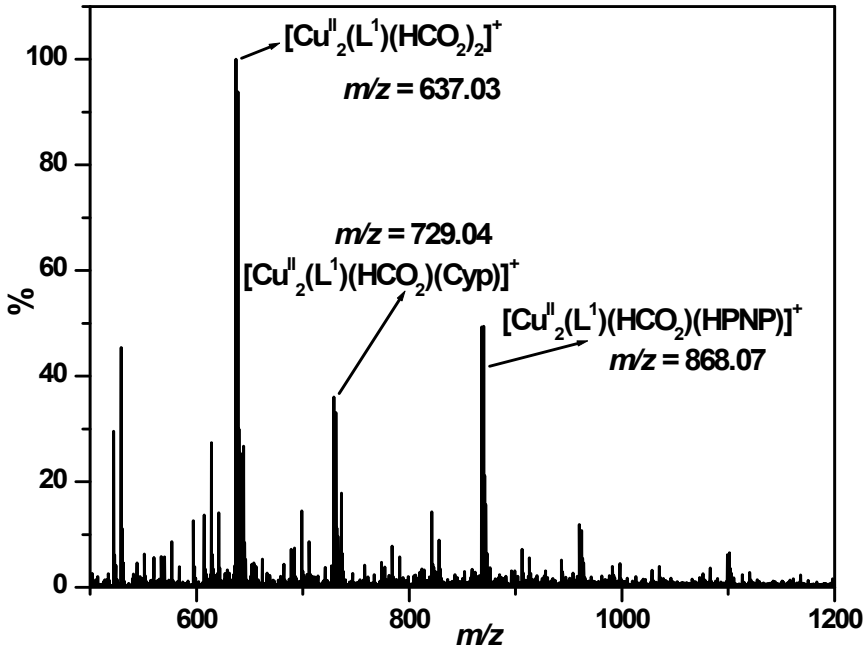


Fig. S11. ESI–MS spectrum of **1** and HPNP (1:30) at pH 8.50 in MeOH–H_2O (33%, v/v).

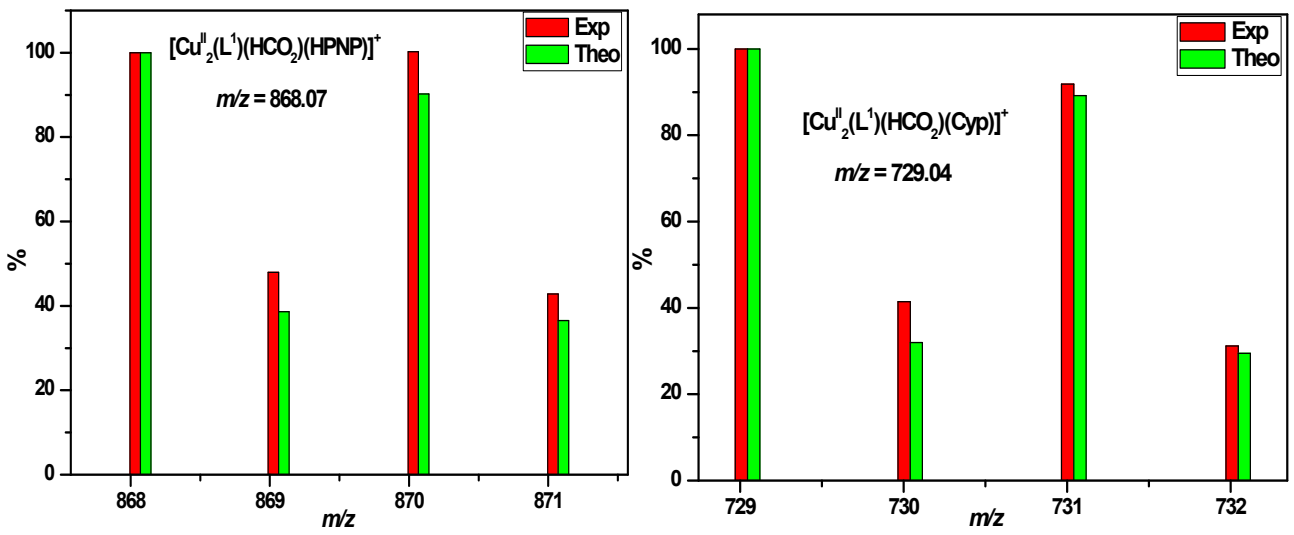


Fig. S12. Simulated (green line) and experimental mass isotopic distribution (red line) for $[Cu^{II}_2(L^1)(HCO_2)(HPNP)]^+$ and $[Cu^{II}_2(L^1)(HCO_2)(Cyp)]^+$.

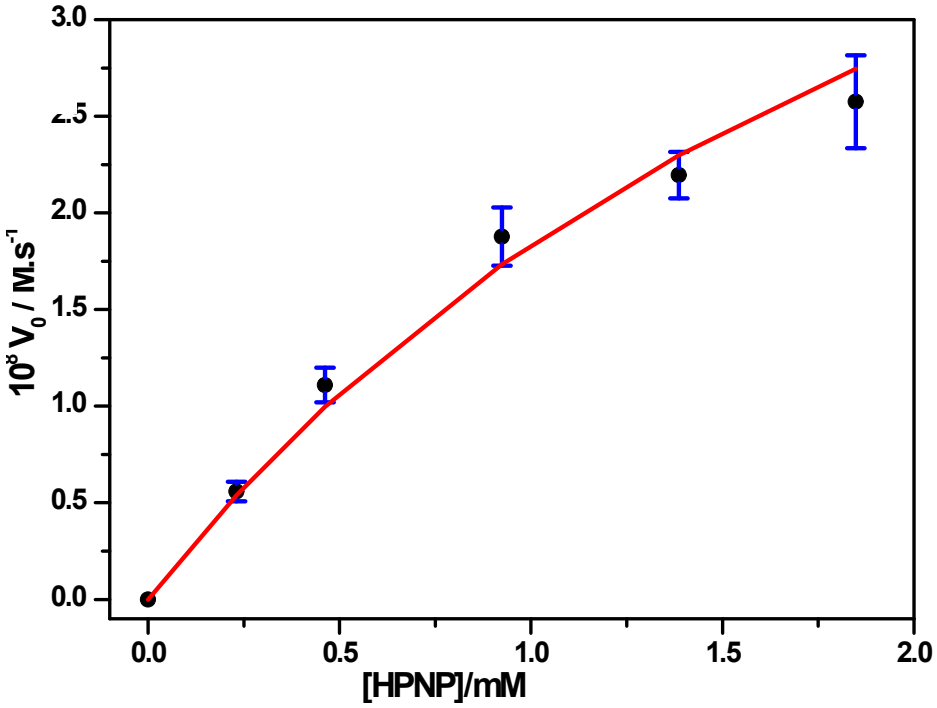


Fig. S13. Dependence of the initial reaction rate (V_0) on the HPNP concentration for the hydrolysis reaction promoted by **1**. Conditions: [complex] = 4.62 × 10^{-5} M; [buffer] = 20 × 10^{-3} M (CHES, pH = 8.50); I = 0.1 M ($NaNO_3$) in MeOH–H_2O (33%, v/v) at 30 °C. V_{max} = 66.1 x 10^{-9} M.s^{-1}, K_M = 2.60 mM.

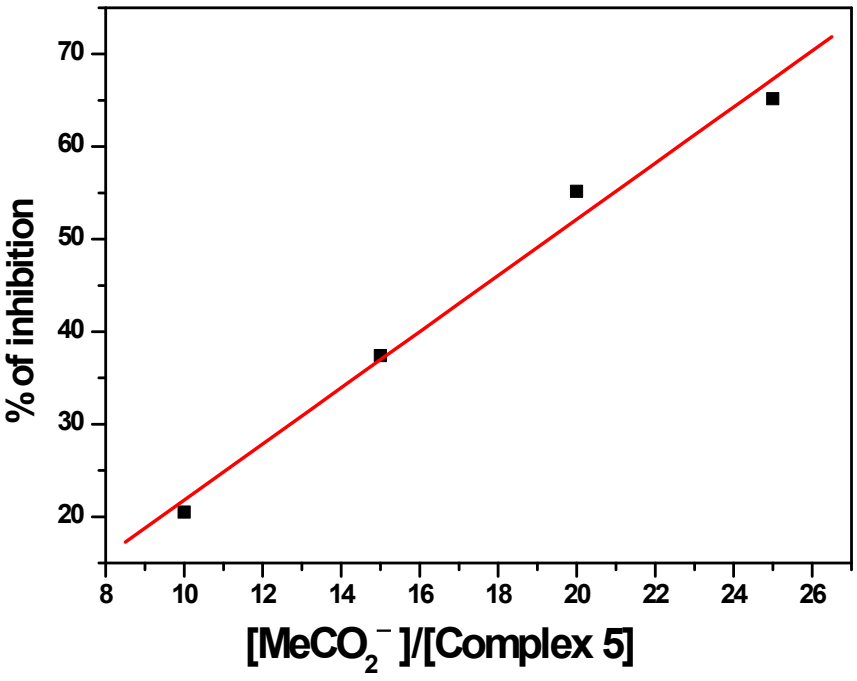
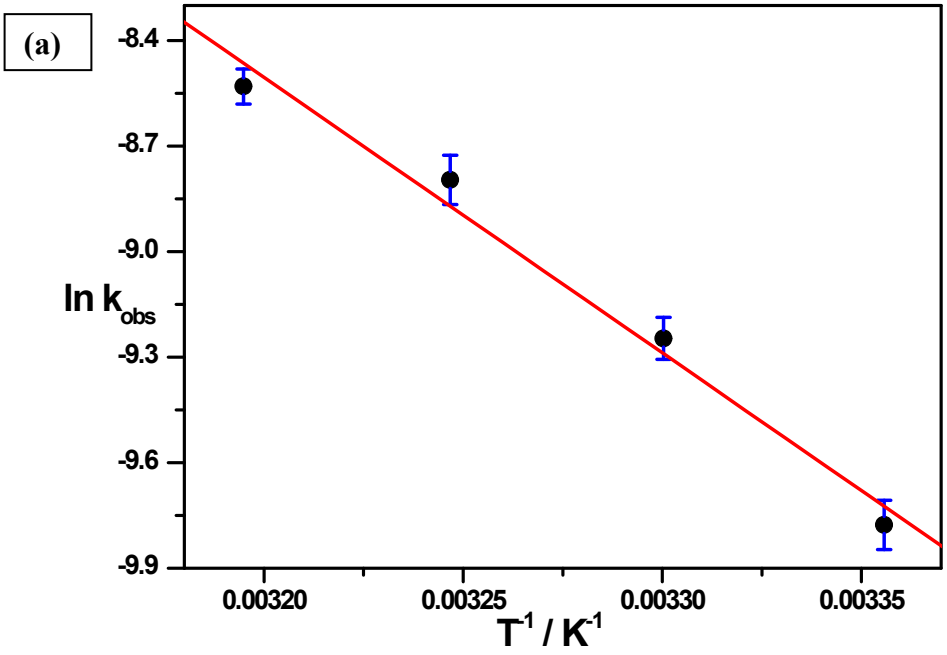


Fig. S14. Percentage inhibitions by acetate ion in hydrolysis of HPNP catalysed by **1**. Conditions: [Complex] = 4.62 × 10^{-5} M, [HPNP] = 4.62 × 10^{-4} M; buffer CHES (pH 8.50), I = 0.1 M ($NaNO_3$) in MeOH–H_2O (33%, v/v) at 30 °C.



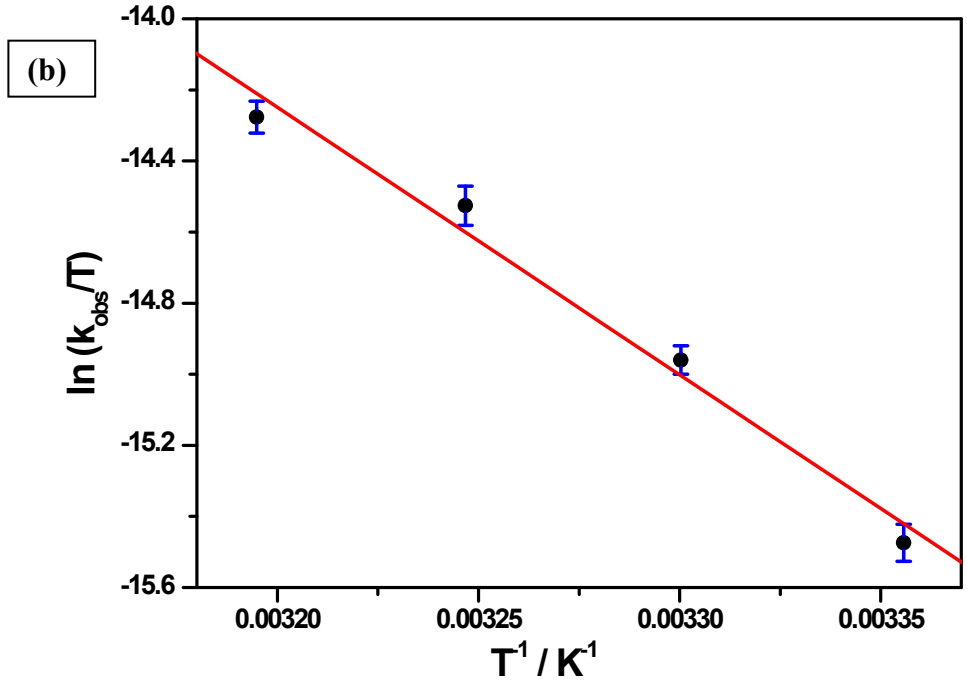
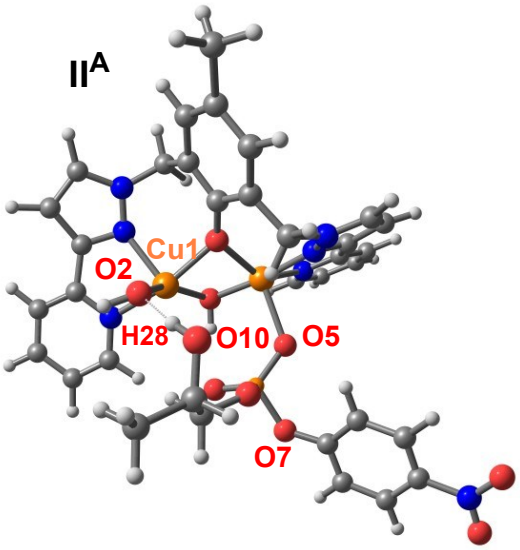
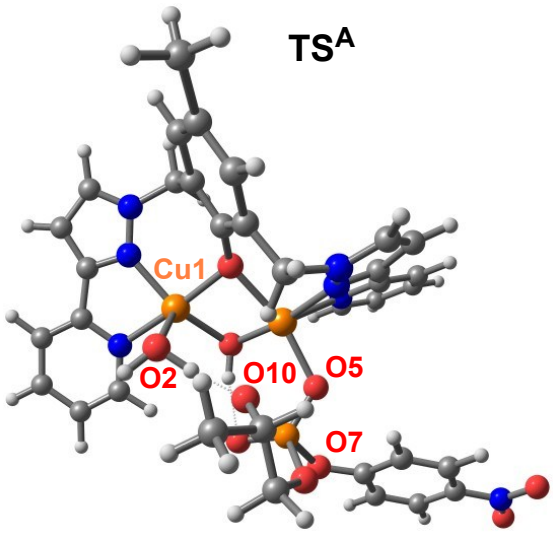


Fig. S15. Linearizations of the observed rate constants for the hydrolysis of HPNP (5×10^{-5} M) promoted by complex **1** (50×10^{-5} M) as a function of temperature: (a) Arrhenius equation and (b) Eyring equation. Conditions: [buffer] = 20×10^{-3} M (CHES, pH = 8.50); I = 0.1 M ($NaNO_3$) in MeOH–H_2O (33%, v/v).



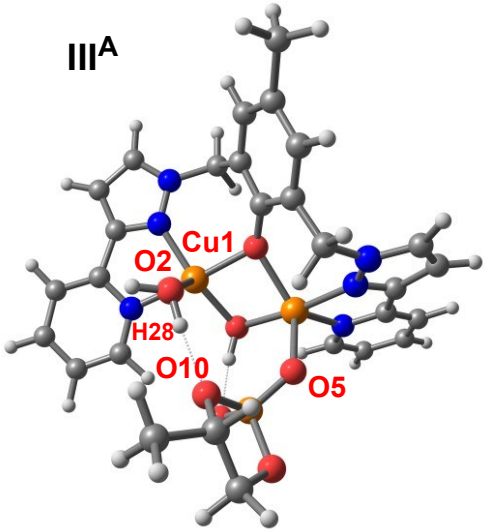
$[Cu^{II}_2(L^1)(\mu\text{-OH})(OH)(HPNP)]$

Cu1-O2 = 1.946, Cu2-O5 = 2.204
O2-H28 = 1.654, O10-H28 = 1.002
O10-P1 = 4.207, P1-O7 = 1.677



$[Cu^{II}_2(L^1)(\mu\text{-OH})(OH)(HPNP)]^{\#}$

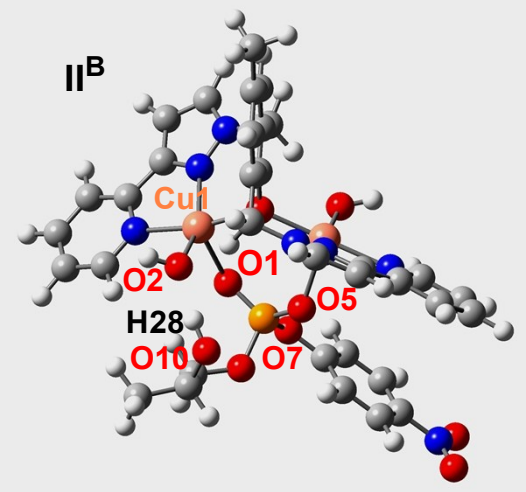
Cu1-O2 = 2.244, Cu2-O5 = 2.025
O2-H28 = 1.033, O10-H28 = 1.506
O10-P1 = 2.281, P1-O7 = 1.768



$[Cu^{II}_2(L^1)(\mu\text{-OH})(H_2O)(Cyp)]^+$

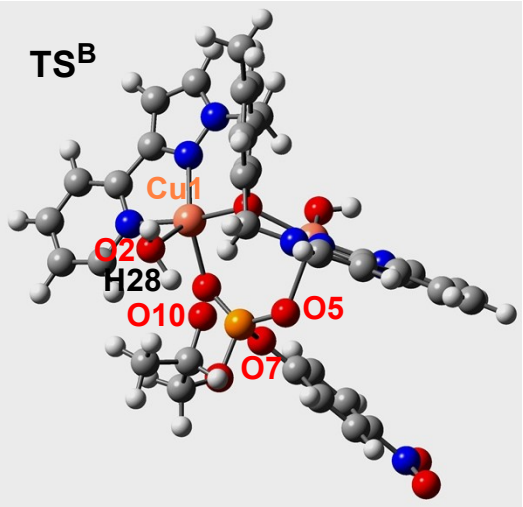
Cu1-O2 = 2.360, Cu2-O5 = 2.165
O2-H28 = 0.977, O10-H28 = 1.826, O10-P1 = 1.663

Fig. S16. Optimized-geometries for the HPNP hydrolysis catalysed by **1**. All distances are given in Å.



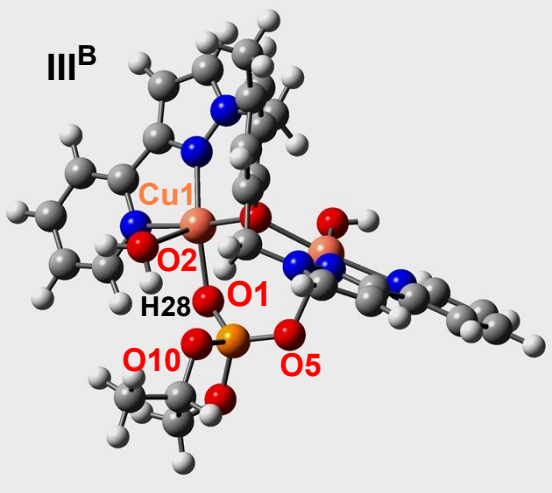
$[Cu^{II}_2(L^1)(OH)_2(HPNP)]$

Cu1-O2 = 1.948, Cu2-O5 = 2.254
O2-H28 = 1.649, O10-H28 = 0.999
O10-P1 = 3.579, P1-O7 = 1.681



$[Cu^{II}_2(L^1)(OH)(H_2O)(HPNP)]^{\#}$

Cu1-O2 = 2.145, Cu2-O5 = 2.240
O2-H28 = 1.080, O10-H28 = 1.380
O10-P1 = 2.286, P1-O7 = 1.783



$[Cu^{II}_2(L^1)(OH)(H_2O)(Cyp)]^{+}$

Cu1-O1 = 2.010, Cu1-O2 = 2.360, Cu2-O5 = 2.326
O2-H28 = 0.973, O10-H28 = 1.983, O10-P1 = 1.660

Fig. S17. Optimized-geometries for the HPNP hydrolysis catalyzed by **4** starting from $\mathbf{I^B}$, where both the hydroxo groups are terminally coordinated. All distances are given in Å.

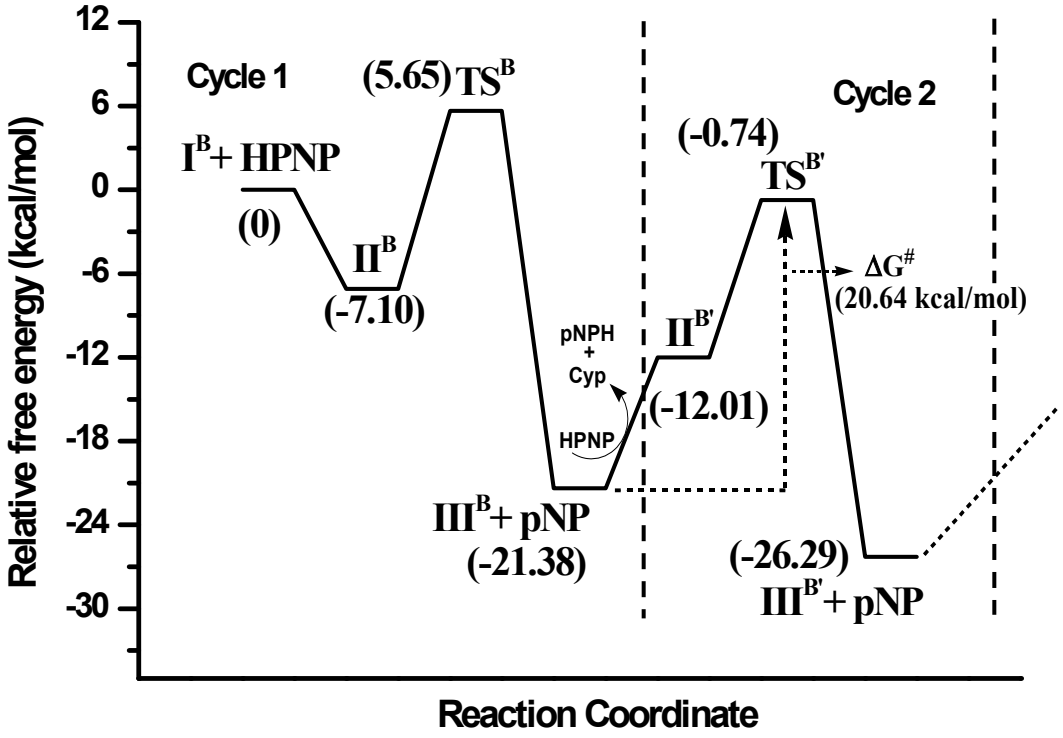


Fig. S18. The free-energy profile for the HPNP hydrolysis catalyzed by **1**, starting from $\mathbf{I^B}$ in presence of excess HPNP.

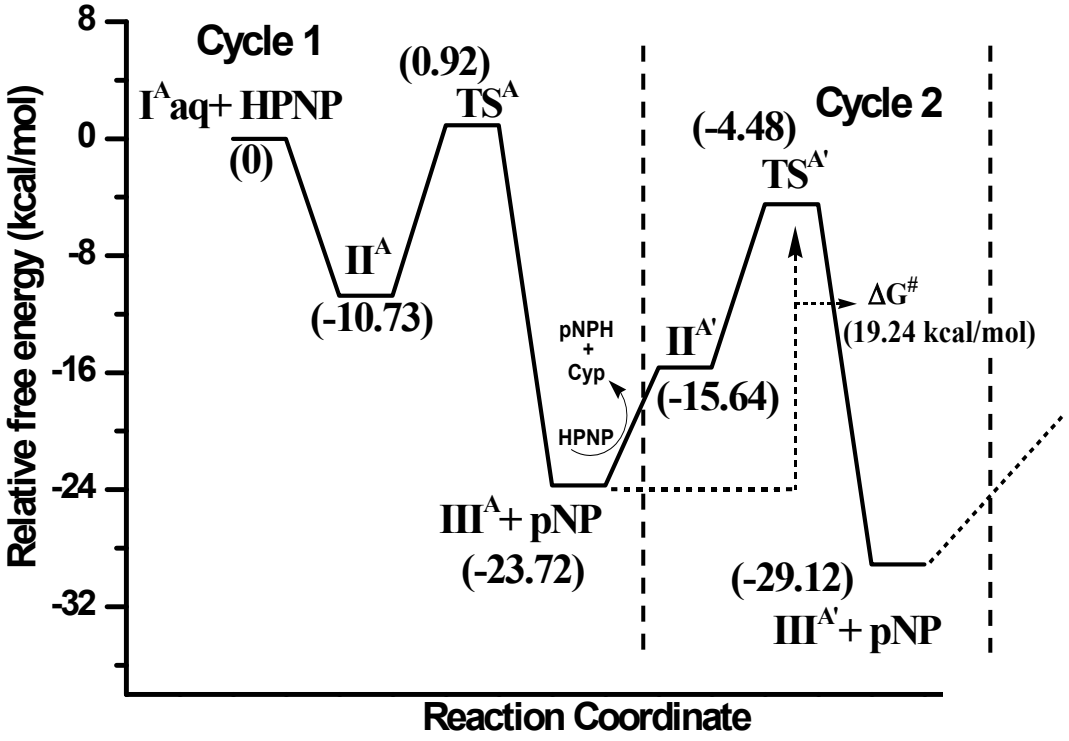


Fig. S19. The free-energy profile for the HPNP hydrolysis catalyzed by **1**, starting from **I^A aq** in presence of excess HPNP.

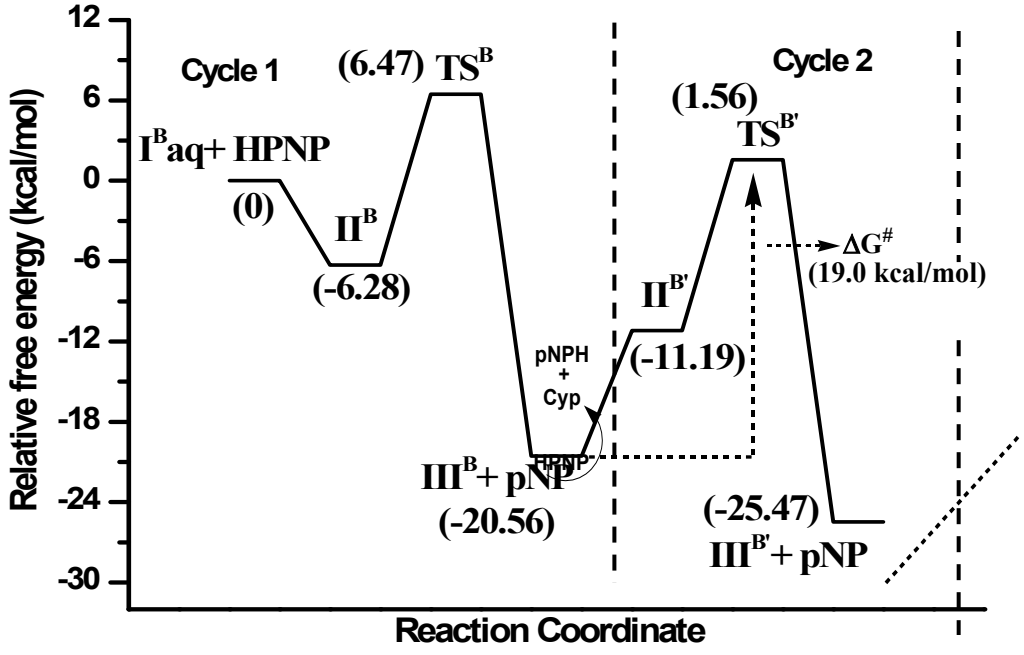


Fig. S20. The free-energy profile for the HPNP hydrolysis catalyzed by **1**, starting from **I^B aq** in presence of excess HPNP**.**

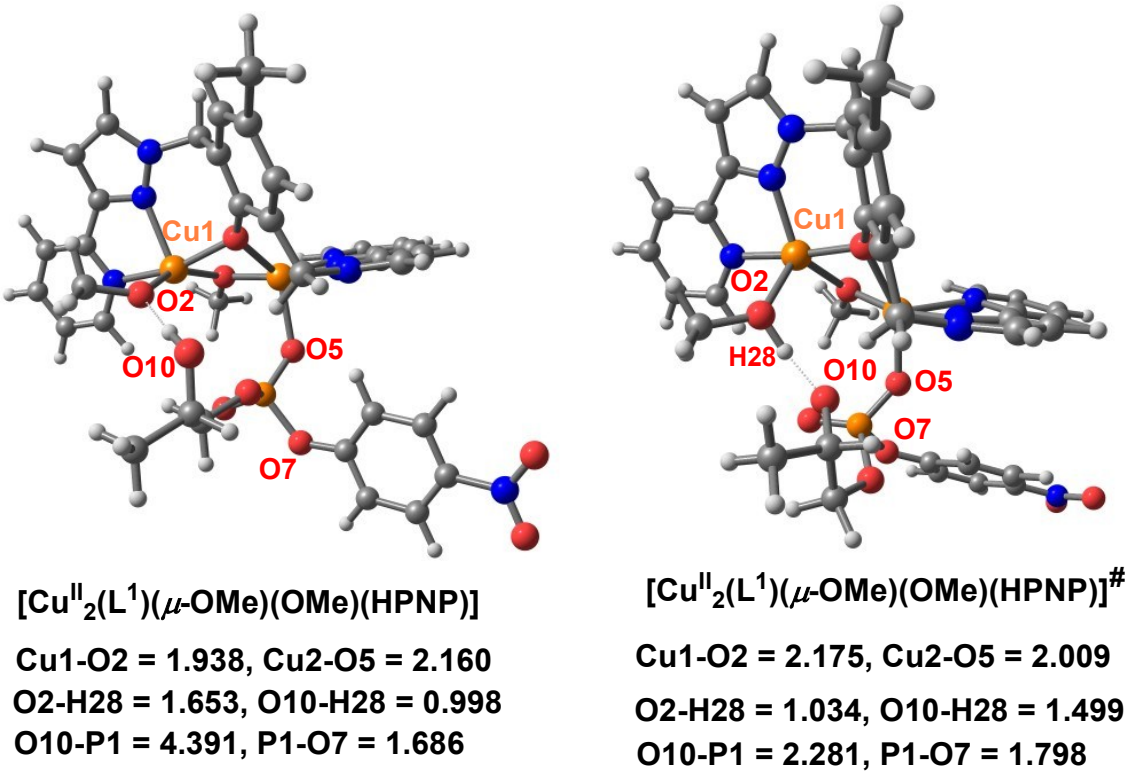


Fig. S21. Optimized-geometries for [Cu$^{II}_2$(L^1)(μ-OMe)(OMe)(HPNP)] (left) and [Cu$^{II}_2$(L^1)(μ-OMe)(OMe)(HPNP)]$^{\#}$ (right).

Table S1 Mulliken spin-density population of **1** in HS and BS state

Atom	HS state	BS state
Cu1	0.620	0.613
Cu2	0.622	–0.614
O1	0.126	0.002
C25	–0.003	–0.002
C27	–0.003	0.002
O2	0.116	0.114
O3	0.000	0.001
O4	0.001	0.002
O5	0.117	–0.115

Table S2 Optimized-coordinates for $[Cu^{II}_2(L^1)(\mu\text{-OH})(OH)]^+$ (**I^A**)

Cu	0.204966000	-0.069304000	-0.162752000
N	0.026950000	-0.013764000	1.919207000
N	2.099876000	-0.076737000	0.356892000
C	2.383838000	-0.058131000	1.667584000
Cu	-1.559616000	-0.208019000	-2.634344000
C	1.348759000	-1.539687000	-2.525248000
C	1.222327000	-0.054368000	2.562219000
C	-1.106401000	0.001777000	2.630190000
N	3.251369000	-0.014870000	-0.313100000
C	3.777052000	0.000686000	1.841333000
O	-1.487971000	0.539869000	-0.825058000
N	-1.314136000	-1.061964000	-4.414790000
N	-1.673614000	1.597014000	-4.534916000
C	-1.489012000	-0.513811000	-5.623165000
C	-1.801985000	0.922520000	-5.696797000
C	0.969289000	-2.761454000	-3.148325000
C	2.738262000	-1.277017000	-2.392017000
C	1.299083000	-0.078230000	3.953524000
N	-0.990300000	-2.349720000	-4.592518000
C	-1.940623000	2.905577000	-4.528449000
C	-1.276800000	-1.497856000	-6.613124000
C	-2.194929000	1.544047000	-6.886541000
C	1.949270000	-3.663361000	-3.574280000
C	-0.477923000	-3.104451000	-3.435667000
C	3.682821000	-2.209114000	-2.830258000
C	3.230996000	0.016302000	-1.787537000
C	-0.946639000	-2.648575000	-5.913476000

C	-2.336875000	3.610595000	-5.667636000
H	-1.830707000	3.412134000	-3.572814000
H	-1.339539000	-1.389778000	-7.684733000
H	-2.293715000	0.969618000	-7.800966000
C	-2.463913000	2.911760000	-6.867488000
H	1.627121000	-4.589389000	-4.045689000
C	3.317755000	-3.423123000	-3.417723000
H	-0.581804000	-4.163454000	-3.674064000
H	-1.139219000	-2.880935000	-2.594566000
H	-0.680414000	-3.638267000	-6.253672000
H	-2.537912000	4.674467000	-5.608652000
H	-2.771461000	3.420888000	-7.775221000
C	4.351097000	-4.433474000	-3.853231000
H	4.008165000	-5.007049000	-4.719248000
H	4.565814000	-5.151421000	-3.051889000
H	5.295375000	-3.948286000	-4.116453000
H	2.264715000	-0.111876000	4.444434000
H	-2.032331000	0.033484000	2.067301000
C	-1.107349000	-0.019695000	4.023681000
H	-2.047266000	-0.004273000	4.562298000
H	4.738053000	-1.970211000	-2.717089000
C	4.292201000	0.027719000	0.549793000
H	5.309370000	0.082646000	0.192020000
H	4.338809000	0.032502000	2.761600000
C	0.115773000	-0.059909000	4.691467000
H	0.151261000	-0.077431000	5.775548000
H	4.255471000	0.221172000	-2.098550000
H	2.602494000	0.861442000	-2.078952000
H	-2.325735000	0.386214000	-0.376828000
O	-3.480841000	-0.390473000	-2.496104000
H	-3.836254000	-0.649597000	-3.353926000
O	0.437177000	-0.649468000	-2.082504000

Table S3 Optimized-coordinates for $[Cu^{II}_2(L^1)(OH)_2]^+$ (**I^B**)

Cu	0.136640000	0.296065000	0.059492000
O	0.155779000	0.376811000	1.954070000
O	2.138984000	0.190908000	0.025936000
N	-1.931061000	0.222190000	-0.260128000
N	0.052958000	0.464828000	-1.962261000
C	-1.180407000	0.586718000	-2.481386000
Cu	3.241047000	-1.385563000	0.592691000
C	2.805484000	1.274589000	-0.425060000
O	2.673690000	-2.347153000	-0.939177000
C	-2.297999000	0.431271000	-1.547882000
C	-2.872077000	0.016327000	0.669194000
N	0.920873000	0.617980000	-2.971602000
C	-1.099015000	0.822723000	-3.863995000
N	4.085366000	-0.318890000	2.100088000
N	4.363781000	-2.872506000	1.549089000

C	4.994479000	-0.980417000	2.835760000
C	5.145538000	-2.409591000	2.554861000
C	3.359412000	2.195611000	0.488309000
C	2.947809000	1.494328000	-1.811190000
C	-3.640492000	0.461440000	-1.926590000
N	4.089095000	0.953132000	2.522179000
C	4.388498000	-4.175052000	1.241360000
C	5.596240000	-0.106530000	3.756618000
C	5.996830000	-3.256654000	3.265140000
C	4.042822000	3.314442000	0.006290000
C	3.156081000	1.954571000	1.965525000
C	3.636464000	2.623738000	-2.259625000
C	2.376730000	0.472351000	-2.765734000
C	4.987191000	1.117933000	3.520584000
C	5.207604000	-5.081774000	1.909770000
H	3.727741000	-4.495895000	0.443877000
H	6.359077000	-0.320766000	4.488550000
H	6.614613000	-2.861619000	4.063024000
C	6.028843000	-4.609766000	2.933490000
H	4.456597000	4.026276000	0.717253000
C	4.196840000	3.549525000	-1.367508000
H	3.329404000	2.866729000	2.537517000
H	2.141143000	1.586905000	2.153528000
H	5.122743000	2.080559000	3.990434000
H	5.195607000	-6.128175000	1.629034000
H	6.682796000	-5.287006000	3.472601000
C	4.964986000	4.748289000	-1.871475000
H	6.024868000	4.505728000	-2.018372000
H	4.917243000	5.579207000	-1.161857000
H	4.575900000	5.096309000	-2.832738000
H	-3.909338000	0.632260000	-2.962357000
H	-2.520550000	-0.169470000	1.677879000
C	-4.231405000	0.026552000	0.365663000
H	-4.960637000	-0.145475000	1.148309000
H	3.746629000	2.783740000	-3.330077000
C	0.262402000	0.834280000	-4.133532000
H	0.802396000	0.972534000	-5.058295000
H	-1.901261000	0.964968000	-4.570982000
C	-4.617993000	0.260088000	-0.953908000
H	-5.668091000	0.278739000	-1.225834000
H	2.824165000	0.570818000	-3.755391000
H	2.546318000	-0.539974000	-2.381896000
H	-0.674585000	0.707402000	2.313301000
H	3.234398000	-3.108435000	-1.123276000

Table S4 Optimized-coordinates for $[Cu^{II}_2(L^1)(\mu\text{-}OH)(OH)(H_2O)]^+$ ($\mathbf{I^A_{aq}}$)

Cu	0.157180000	-0.255902000	-0.154531000
N	0.020284000	0.106960000	1.911035000
N	2.079617000	-0.025481000	0.317678000
C	2.372943000	0.139935000	1.615568000
Cu	-1.590651000	-0.259184000	-2.650787000
C	1.323238000	-1.559369000	-2.580008000
C	1.226131000	0.178756000	2.527790000
C	-1.099200000	0.157228000	2.640715000
N	3.221551000	0.043328000	-0.367534000
C	3.762071000	0.301986000	1.766569000
O	-1.566175000	0.367943000	-0.798546000
N	-1.295423000	-0.977312000	-4.486342000
N	-1.699074000	1.679166000	-4.430080000
C	-1.425773000	-0.344108000	-5.657911000
C	-1.766573000	1.087710000	-5.641194000
C	0.955237000	-2.764926000	-3.242250000
C	2.711778000	-1.302894000	-2.413283000
C	1.328831000	0.302487000	3.913190000
N	-0.935507000	-2.241986000	-4.742846000
C	-1.998389000	2.977691000	-4.340816000
C	-1.146556000	-1.247816000	-6.706427000
C	-2.127426000	1.785399000	-6.798511000
C	1.943160000	-3.672408000	-3.642011000
C	-0.479887000	-3.076321000	-3.617699000
C	3.662283000	-2.238348000	-2.828169000
C	3.191865000	0.009782000	-1.840895000
C	-0.824268000	-2.441334000	-6.078579000
C	-2.367597000	3.754700000	-5.441626000
H	-1.937984000	3.415329000	-3.347432000
H	-1.161814000	-1.061232000	-7.768957000
H	-2.177108000	1.276722000	-7.754909000
C	-2.430135000	3.142015000	-6.692681000
H	1.630396000	-4.586901000	-4.141347000
C	3.306295000	-3.449140000	-3.430014000
H	-0.577085000	-4.116926000	-3.929094000
H	-1.183565000	-2.903912000	-2.799017000
H	-0.522810000	-3.398217000	-6.478044000
H	-2.597356000	4.806797000	-5.314903000
H	-2.714529000	3.708801000	-7.573404000
C	4.347315000	-4.464369000	-3.834886000
H	3.982139000	-5.112000000	-4.636865000
H	4.620441000	-5.110386000	-2.991299000
H	5.264859000	-3.977726000	-4.179296000
H	2.303614000	0.357287000	4.383830000
H	-2.034976000	0.098143000	2.095877000
C	-1.076061000	0.281740000	4.028899000
H	-2.006262000	0.321574000	4.583104000
H	4.715633000	-2.004447000	-2.689024000
C	4.264994000	0.238061000	0.473133000

H	5.273125000	0.327832000	0.097250000
H	4.326321000	0.457934000	2.672648000
C	0.159641000	0.353001000	4.671283000
H	0.215175000	0.448414000	5.750524000
H	4.212824000	0.213860000	-2.164429000
H	2.552044000	0.835344000	-2.163064000
H	-2.398221000	0.131061000	-0.376436000
O	-3.510874000	-0.501168000	-2.567057000
H	-3.835783000	-0.718681000	-3.448238000
O	0.413550000	-0.676981000	-2.126547000
O	0.037591000	-2.569126000	0.403373000
H	0.290400000	-3.234404000	-0.247628000
H	-0.757931000	-2.906558000	0.831895000

Table S5 Optimized-coordinates for $[Cu^{II}_2(L^1)(OH)_2(H_2O)]^+$ ($\mathbf{I^B_{aq}}$)

Cu	-0.009809000	0.045453000	0.078789000
O	0.051037000	0.096011000	2.374677000
O	1.879448000	0.122092000	-0.309204000
O	0.087313000	-2.004552000	-0.000490000
N	-0.478835000	2.105613000	-0.269739000
N	-2.051344000	0.025727000	0.132530000
C	-2.658911000	1.219620000	0.053141000
Cu	1.315046000	-3.138948000	1.203807000
C	-0.636362000	-2.619920000	-0.955053000
O	0.426393000	-2.438144000	2.765339000
C	-1.802825000	2.381151000	-0.192509000
C	0.380167000	3.103291000	-0.509044000
N	-3.004495000	-0.882442000	0.375357000
C	-4.044830000	1.068407000	0.241620000
N	2.138678000	-4.111361000	-0.382497000
N	2.248455000	-4.816213000	2.149769000
C	2.937334000	-5.151364000	-0.095478000
C	2.987127000	-5.574423000	1.305030000
C	-0.031520000	-3.055210000	-2.156247000
C	-2.022645000	-2.830938000	-0.777605000
C	-2.292526000	3.679628000	-0.346198000
N	2.246698000	-3.885381000	-1.696991000
C	2.196761000	-5.143398000	3.445935000
C	3.567641000	-5.610438000	-1.266116000
C	3.714161000	-6.677579000	1.756102000
C	-0.801789000	-3.690895000	-3.132971000
C	1.448302000	-2.829634000	-2.348841000
C	-2.764178000	-3.471787000	-1.772590000
C	-2.676596000	-2.317276000	0.481062000
C	3.093584000	-4.774449000	-2.266502000
C	2.891852000	-6.230448000	3.971799000
H	1.572797000	-4.520980000	4.077327000
H	4.264813000	-6.425808000	-1.378704000
H	4.298065000	-7.266535000	1.058378000

C	3.667829000	-7.004862000	3.109515000
H	-0.320127000	-4.012499000	-4.054106000
C	-2.174242000	-3.917769000	-2.962946000
H	1.720046000	-2.857651000	-3.404689000
H	1.755648000	-1.871272000	-1.921671000
H	3.292299000	-4.749808000	-3.327490000
H	2.820763000	-6.457129000	5.029017000
H	4.225215000	-7.857264000	3.483405000
C	-2.984285000	-4.637185000	-4.015241000
H	-2.999603000	-5.719062000	-3.833097000
H	-2.566621000	-4.482344000	-5.014290000
H	-4.023280000	-4.295021000	-4.022351000
H	-3.357406000	3.869451000	-0.279722000
H	1.429079000	2.838433000	-0.576690000
C	-0.030268000	4.424310000	-0.673470000
H	0.704006000	5.197872000	-0.864580000
H	-3.829542000	-3.627630000	-1.615995000
C	-4.221374000	-0.292677000	0.440684000
H	-5.112268000	-0.875888000	0.620056000
H	-4.811023000	1.827771000	0.236910000
C	-1.391684000	4.714378000	-0.586697000
H	-1.748803000	5.731585000	-0.708254000
H	-3.620753000	-2.826491000	0.676622000
H	-2.015997000	-2.440983000	1.342419000
H	2.257666000	0.999679000	-0.195025000
H	0.816128000	0.575648000	2.709653000
H	0.209217000	-0.884220000	2.580550000
H	0.945219000	-2.578906000	3.564528000
O	3.060897000	-1.641533000	1.171700000
H	3.211301000	-1.265321000	2.045552000
H	2.647006000	-0.907387000	0.607782000

Table S6 Optimized-coordinates for $[Cu^{II}_2(L^1)(\mu\text{-OH})(OH)(HPNP)]$ (**II^A**)

Cu	-0.569637000	-0.063745000	0.038782000
O	-0.514638000	0.145696000	3.640833000
O	1.206489000	0.596668000	-0.406038000
O	-0.210788000	-2.012598000	-0.508757000
N	-1.361254000	1.882956000	0.270086000
N	-1.711270000	0.293266000	-1.850492000
C	-1.827507000	1.609204000	-2.059980000
Cu	-0.834555000	-2.753217000	1.299336000
C	0.431166000	-2.489697000	-1.579367000
O	-1.791829000	-1.062992000	1.303833000
C	-1.832638000	2.462878000	-0.862108000
C	-1.358508000	2.569281000	1.420929000
N	-1.634682000	-0.284941000	-3.048273000
C	-1.855317000	1.879694000	-3.447212000
N	0.192939000	-4.426068000	1.052377000
N	-2.220981000	-4.286558000	2.048852000

C	-0.326656000	-5.590069000	1.461991000
C	-1.675291000	-5.526213000	2.041692000
C	1.641077000	-3.221507000	-1.449030000
C	-0.094259000	-2.298719000	-2.889633000
C	-2.294144000	3.781960000	-0.857478000
N	1.407364000	-4.669170000	0.552879000
C	-3.446709000	-4.111131000	2.549370000
C	0.596289000	-6.624929000	1.212663000
C	-2.362103000	-6.632016000	2.545045000
C	2.328789000	-3.654969000	-2.586013000
C	2.176661000	-3.577103000	-0.079949000
C	0.632387000	-2.745176000	-3.997792000
C	-1.490450000	-1.748642000	-3.118792000
C	1.685993000	-5.993263000	0.627533000
C	-4.198579000	-5.164944000	3.069877000
H	-3.829767000	-3.095339000	2.529151000
H	0.496989000	-7.678153000	1.424271000
H	-1.904063000	-7.614457000	2.529874000
C	-3.642256000	-6.443893000	3.065854000
H	3.258827000	-4.204211000	-2.454414000
C	1.861054000	-3.405204000	-3.880292000
H	3.205957000	-3.931099000	-0.147460000
H	2.151914000	-2.725266000	0.602644000
H	2.624533000	-6.385221000	0.264788000
H	-5.190431000	-4.980777000	3.466073000
H	-4.196762000	-7.287564000	3.463396000
C	2.641857000	-3.836867000	-5.098586000
H	1.976547000	-4.086504000	-5.930727000
H	3.264038000	-4.710920000	-4.885031000
H	3.310087000	-3.039052000	-5.446505000
H	-2.671809000	4.225308000	-1.771920000
H	-0.980120000	2.036300000	2.289365000
C	-1.809853000	3.885822000	1.498478000
H	-1.789469000	4.409881000	2.447039000
H	0.209664000	-2.593837000	-4.989130000
C	-1.724011000	0.634224000	-4.045306000
H	-1.693948000	0.342064000	-5.084645000
H	-1.941276000	2.832879000	-3.946391000
C	-2.276963000	4.500773000	0.336206000
H	-2.633271000	5.525518000	0.359213000
H	-1.840063000	-2.043611000	-4.109503000
H	-2.182425000	-2.151848000	-2.375603000
H	1.182717000	1.551024000	-0.532367000
H	-1.707011000	-0.635808000	2.172114000
O	0.059007000	-2.386181000	3.280908000
P	0.417248000	-1.018648000	3.828848000
O	1.928883000	-0.701168000	3.342083000
O	0.593483000	-1.159056000	5.489701000
C	1.324178000	-2.068086000	6.186737000
C	1.268642000	-1.946736000	7.586588000
C	2.101971000	-3.076231000	5.590851000
C	1.982519000	-2.819356000	8.390280000

H	0.660846000	-1.161362000	8.021360000
C	2.818852000	-3.952261000	6.394774000
H	2.135390000	-3.175835000	4.513857000
C	2.755778000	-3.819225000	7.785758000
H	1.947995000	-2.735613000	9.468938000
H	3.424046000	-4.733558000	5.952766000
N	3.509032000	-4.738004000	8.622163000
O	3.448249000	-4.605711000	9.846550000
O	4.181491000	-5.616475000	8.077815000
C	2.406850000	0.621687000	3.017785000
C	3.629856000	0.497446000	2.106038000
O	3.350551000	-0.227919000	0.918098000
H	2.541899000	0.135120000	0.454743000
H	1.611817000	1.182412000	2.517558000
H	5.083387000	1.803946000	1.176449000
C	4.196352000	1.891667000	1.809552000
H	4.482379000	2.411409000	2.730367000
H	3.459380000	2.508399000	1.282239000
H	2.680565000	1.141927000	3.942852000
H	4.389826000	-0.088122000	2.639320000

Table S7 Optimized-coordinates for $[Cu^{II}_2(L^1)(OH)_2(HPNP)]$ **(II^B)**

Cu	-0.562971000	0.006060000	-0.122827000
O	-1.014154000	-0.247925000	2.087768000
O	1.377134000	0.123139000	0.003001000
O	-0.599944000	-1.987330000	-0.548592000
N	-0.876109000	2.092035000	0.053831000
N	-2.421537000	0.257113000	-1.027268000
C	-2.899299000	1.513468000	-1.034847000
Cu	-0.717879000	-3.659445000	0.645913000
C	-0.569056000	-2.264195000	-1.867618000
O	-2.643831000	-3.604194000	0.722737000
C	-2.074495000	2.535354000	-0.388455000
C	-0.034610000	2.944133000	0.647948000
N	-3.289988000	-0.491050000	-1.719754000
C	-4.116459000	1.565156000	-1.736776000
N	1.139742000	-4.305243000	-0.042899000
N	-0.493056000	-5.515840000	1.642211000
C	1.545133000	-5.497166000	0.426064000
C	0.673938000	-6.155789000	1.402335000
C	0.649674000	-2.597153000	-2.500641000
C	-1.755473000	-2.226043000	-2.636511000
C	-2.459900000	3.869405000	-0.237502000
N	2.059890000	-3.904313000	-0.929549000
C	-1.348737000	-6.016407000	2.539729000
C	2.765978000	-5.862409000	-0.170254000

C	1.001919000	-7.344583000	2.059042000
C	0.667191000	-2.864548000	-3.872374000
C	1.911225000	-2.635306000	-1.670201000
C	-1.701070000	-2.501127000	-4.004956000
C	-3.064154000	-1.933357000	-1.940072000
C	3.055148000	-4.816553000	-1.033961000
C	-1.092708000	-7.196648000	3.235076000
H	-2.257265000	-5.446564000	2.702654000
H	3.352019000	-6.754246000	-0.011849000
H	1.944200000	-7.838640000	1.852220000
C	0.103191000	-7.870611000	2.984738000
H	1.615183000	-3.106478000	-4.348606000
C	-0.497742000	-2.821777000	-4.649939000
H	2.797011000	-2.559517000	-2.302565000
H	1.908173000	-1.812901000	-0.947195000
H	3.885022000	-4.658427000	-1.706489000
H	-1.814689000	-7.570765000	3.951555000
H	0.337040000	-8.792120000	3.507692000
C	-0.465602000	-3.140396000	-6.126410000
H	-0.716988000	-4.192154000	-6.312295000
H	0.526997000	-2.963103000	-6.550078000
H	-1.186975000	-2.533460000	-6.681913000
H	-3.427595000	4.200322000	-0.596318000
H	0.909213000	2.522560000	0.974118000
C	-0.345648000	4.289780000	0.833213000
H	0.365544000	4.948446000	1.317758000
H	-2.622364000	-2.472305000	-4.583511000
C	-4.325036000	0.261183000	-2.161352000
H	-5.122325000	-0.179522000	-2.741056000
H	-4.747939000	2.418999000	-1.926727000
C	-1.581443000	4.755532000	0.382980000
H	-1.859320000	5.796389000	0.512346000
H	-3.906922000	-2.269453000	-2.546166000
H	-3.088387000	-2.438866000	-0.966862000
H	1.709331000	0.834068000	-0.555876000
H	-2.999060000	-4.497731000	0.782544000
O	-0.098065000	-2.659960000	2.569214000
P	-0.465737000	-1.277070000	3.041757000
O	0.736593000	-0.674875000	3.954561000
O	-1.666888000	-1.425562000	4.207808000
C	-1.711559000	-2.293584000	5.248711000
C	-2.956643000	-2.418438000	5.891489000
C	-0.601540000	-3.027242000	5.704647000
C	-3.099636000	-3.269121000	6.974678000
H	-3.797131000	-1.841050000	5.523380000
C	-0.742622000	-3.882513000	6.788597000
H	0.358068000	-2.926424000	5.214960000
C	-1.988054000	-3.999778000	7.415265000
H	-4.053644000	-3.375851000	7.474961000
H	0.102106000	-4.453897000	7.151828000
N	-2.131791000	-4.899340000	8.546058000
O	-3.231486000	-4.982310000	9.098069000

O	-1.149945000	-5.548889000	8.913454000
C	1.479421000	0.516081000	3.615187000
C	2.899174000	0.174272000	3.154417000
O	2.906718000	-0.664432000	2.009056000
H	2.336519000	-0.291031000	1.278527000
H	0.942654000	1.068380000	2.839338000
H	4.722930000	1.210151000	2.624108000
C	3.703904000	1.460735000	2.931346000
H	3.759599000	2.062467000	3.844890000
H	3.253029000	2.074915000	2.143454000
H	1.518898000	1.125872000	4.522643000
H	3.378673000	-0.408570000	3.951391000

Table 8 Optimized-coordinates for $[Cu^{II}_2(L^1)(\mu\text{-OH})(OH)(HPNP)]^{\#}$ (**TS^A**)

Cu	-2.516940000	-0.726717000	-0.802275000
O	0.527510000	-3.010360000	0.688769000
O	-2.665981000	-0.910395000	1.429441000
O	-1.721216000	1.133993000	-0.631043000
N	-3.457428000	-2.592372000	-1.037911000
N	-4.255692000	-0.189786000	-1.649414000
C	-5.149773000	-1.162651000	-1.878898000
Cu	0.226554000	0.376657000	-0.379466000
C	-2.407236000	2.178352000	-0.129778000
O	-0.632107000	-1.202993000	-1.096250000
C	-4.732436000	-2.514592000	-1.491604000
C	-2.951385000	-3.775437000	-0.671852000
N	-4.753413000	0.942417000	-2.148178000
C	-6.275471000	-0.623584000	-2.529268000
N	0.876107000	2.164985000	0.189087000
N	1.838498000	1.219367000	-2.105522000
C	1.848595000	2.872065000	-0.397233000
C	2.465286000	2.306621000	-1.606994000
C	-2.053093000	2.816643000	1.092165000
C	-3.530600000	2.691433000	-0.833875000
C	-5.538976000	-3.648734000	-1.590055000
N	0.413322000	2.877660000	1.220632000
C	2.333765000	0.644312000	-3.203866000
C	2.023553000	4.085469000	0.302279000
C	3.605852000	2.851575000	-2.204173000
C	-2.828008000	3.874089000	1.578330000
C	-0.822153000	2.417360000	1.878244000
C	-4.279052000	3.747571000	-0.305809000
C	-3.909186000	2.151576000	-2.192208000
C	1.078812000	4.053626000	1.318345000
C	3.466445000	1.120920000	-3.868138000
H	1.801854000	-0.231713000	-3.566304000
H	2.723730000	4.880104000	0.096510000
H	4.089236000	3.722076000	-1.774560000

C	4.110288000	2.246457000	-3.354525000
H	-2.532606000	4.339034000	2.516647000
C	-3.961151000	4.352576000	0.912515000
H	-0.840940000	2.866599000	2.871977000
H	-0.726395000	1.332032000	1.984364000
H	0.832659000	4.772410000	2.085644000
H	3.827705000	0.620237000	-4.759444000
H	4.995034000	2.647143000	-3.838747000
C	-4.800810000	5.468313000	1.486247000
H	-5.564357000	5.079070000	2.171317000
H	-5.321944000	6.019794000	0.698346000
H	-4.189536000	6.177358000	2.052485000
H	-6.557095000	-3.563978000	-1.952135000
H	-1.927834000	-3.770139000	-0.309224000
C	-3.696065000	-4.951746000	-0.747400000
H	-3.251325000	-5.892977000	-0.446474000
H	-5.129131000	4.116359000	-0.876071000
C	-5.976517000	0.723494000	-2.688127000
H	-6.531989000	1.525472000	-3.150789000
H	-7.169950000	-1.130749000	-2.855544000
C	-5.009233000	-4.882359000	-1.212717000
H	-5.617424000	-5.778193000	-1.280915000
H	-4.482562000	2.893286000	-2.748933000
H	-3.019554000	1.892056000	-2.772272000
H	-3.108864000	-1.699797000	1.756928000
H	-0.320871000	-1.973536000	-0.579600000
O	1.757952000	-0.652261000	0.456049000
P	1.496857000	-1.971900000	1.211410000
O	1.964644000	-2.039064000	2.779097000
O	2.988386000	-2.801766000	0.749661000
C	4.248004000	-2.380245000	0.854003000
C	5.244202000	-3.253023000	0.352865000
C	4.640694000	-1.146576000	1.425446000
C	6.582080000	-2.916159000	0.419463000
H	4.932569000	-4.195666000	-0.083679000
C	5.981408000	-0.806795000	1.493465000
H	3.889525000	-0.467427000	1.803900000
C	6.950984000	-1.688265000	0.993143000
H	7.342980000	-3.585060000	0.037450000
H	6.287266000	0.135163000	1.931615000
N	8.344529000	-1.329192000	1.068855000
O	9.188948000	-2.115472000	0.621540000
O	8.656160000	-0.245549000	1.578654000
C	1.038565000	-1.852021000	3.863109000
C	0.117613000	-0.681587000	3.522205000
O	-0.246332000	-0.870771000	2.188036000
H	-1.699695000	-0.929028000	1.795129000
H	0.455343000	-2.773186000	3.991091000
H	-1.715944000	0.231163000	4.254284000
C	-1.065482000	-0.615484000	4.492976000
H	-0.719482000	-0.493507000	5.526227000
H	-1.663679000	-1.532247000	4.436337000

H	1.648423000	-1.683772000	4.754695000
H	0.707593000	0.251357000	3.636880000

Table S9 Optimized-coordinates for $[Cu^{II}_2(L^1)(OH)_2(HPNP)]^{\#}$ (**TS^B**)

Cu	-2.239771000	-0.771302000	0.072810000
O	-0.541147000	-1.884566000	0.469668000
O	-2.626444000	-0.544630000	2.170338000
O	-1.362432000	1.021968000	-0.160498000
N	-3.335351000	-2.558189000	0.080944000
N	-3.462743000	-0.552167000	-1.569750000
C	-4.342557000	-1.541823000	-1.797182000
Cu	0.631209000	1.372492000	-0.643875000
C	-2.161464000	2.108473000	-0.173205000
O	0.330888000	0.611897000	-2.379263000
C	-4.285153000	-2.676272000	-0.873408000
C	-3.167622000	-3.529384000	0.981886000
N	-3.657430000	0.371668000	-2.514426000
C	-5.124926000	-1.236356000	-2.924802000
N	0.808327000	2.846333000	0.804571000
N	2.566027000	2.175684000	-1.046417000
C	1.952962000	3.546462000	0.793853000
C	2.942807000	3.180340000	-0.221829000
C	-2.201939000	2.982283000	0.939662000
C	-2.943339000	2.423601000	-1.311210000
C	-5.110193000	-3.800154000	-0.943409000
N	0.075516000	3.314795000	1.820218000
C	3.420567000	1.733525000	-1.975653000
C	1.947906000	4.495493000	1.834098000
C	4.196735000	3.786070000	-0.333893000
C	-3.053958000	4.090029000	0.924185000
C	-1.260009000	2.753079000	2.098121000
C	-3.781099000	3.540781000	-1.291562000
C	-2.811260000	1.577314000	-2.555503000
C	0.725414000	4.313929000	2.463445000
C	4.690156000	2.282178000	-2.145557000
H	3.077057000	0.910379000	-2.592996000
H	2.713041000	5.208786000	2.097785000
H	4.474026000	4.591329000	0.336538000
C	5.078741000	3.330811000	-1.311405000
H	-3.075281000	4.746589000	1.791495000
C	-3.870847000	4.383175000	-0.174963000
H	-1.614739000	3.253080000	3.000394000
H	-1.113645000	1.690650000	2.305181000
H	0.278282000	4.813362000	3.309960000
H	5.349880000	1.892863000	-2.912099000
H	6.058337000	3.785436000	-1.415915000
C	-4.814309000	5.561793000	-0.158871000
H	-4.458117000	6.349079000	0.511546000
H	-5.812170000	5.264987000	0.187610000
H	-4.933463000	5.990686000	-1.158274000

H	-5.865711000	-3.876069000	-1.716878000
H	-2.381105000	-3.366419000	1.708931000
C	-3.951903000	-4.681966000	0.976339000
H	-3.788541000	-5.451726000	1.721483000
H	-4.369892000	3.769508000	-2.177508000
C	-4.652593000	-0.002384000	-3.351807000
H	-4.944672000	0.623666000	-4.181723000
H	-5.915286000	-1.818803000	-3.371920000
C	-4.938048000	-4.813981000	-0.001943000
H	-5.566882000	-5.697650000	-0.034274000
H	-3.127787000	2.134711000	-3.438108000
H	-1.773174000	1.244411000	-2.678817000
H	-3.063526000	0.266068000	2.449735000
H	0.957954000	0.953124000	-3.025414000
O	1.510424000	-0.179527000	0.711328000
P	0.837040000	-1.505312000	1.004396000
O	1.419189000	-2.400099000	2.249102000
O	1.723191000	-2.553296000	-0.134009000
C	3.036779000	-2.635091000	-0.319544000
C	3.472290000	-3.437175000	-1.404051000
C	4.006755000	-1.991162000	0.487524000
C	4.816710000	-3.594355000	-1.677372000
H	2.722869000	-3.927094000	-2.016284000
C	5.355027000	-2.146579000	0.214466000
H	3.689822000	-1.374059000	1.316498000
C	5.761826000	-2.945280000	-0.865046000
H	5.147006000	-4.207508000	-2.506435000
H	6.099452000	-1.657147000	0.830185000
N	7.165365000	-3.101576000	-1.144061000
O	7.509942000	-3.812972000	-2.096999000
O	7.987854000	-2.520281000	-0.424101000
C	0.772954000	-2.459572000	3.532986000
C	0.313133000	-1.052315000	3.916215000
O	-0.245867000	-0.513051000	2.756621000
H	-0.087826000	-3.137737000	3.462110000
H	-0.954204000	-0.062394000	5.371528000
C	-0.638426000	-1.078439000	5.114653000
H	-0.151967000	-1.513489000	5.995546000
H	-1.533647000	-1.668898000	4.889340000
H	1.509196000	-2.883331000	4.221229000
H	1.211193000	-0.471641000	4.202769000
H	-1.606719000	-0.539452000	2.528614000

Table S10 Optimized-coordinates for $[Cu^{II}_2(L^1)(\mu\text{-}OH)(H_2O)(Cyp)]$ (**III^A**)

Cu	-0.641692000	0.048964000	-0.267273000
O	-0.303041000	-0.080820000	3.661692000
O	1.685814000	0.002283000	0.124334000
O	-0.591091000	-1.893201000	-0.796108000
N	-0.576807000	2.091250000	0.178482000
N	-0.713443000	0.843372000	-2.098572000
C	-0.634018000	2.178475000	-2.190623000
Cu	-1.235171000	-2.514178000	1.137303000
C	0.124487000	-2.425949000	-1.801285000
O	-1.674795000	-0.646358000	1.269507000
C	-0.511904000	2.892773000	-0.914375000
C	-0.483217000	2.621608000	1.403656000
N	-0.912497000	0.360257000	-3.324564000
C	-0.764043000	2.562590000	-3.538436000
N	-0.797082000	-4.378001000	0.766695000
N	-3.024096000	-3.567217000	1.795969000
C	-1.663908000	-5.356223000	1.046202000
C	-2.932371000	-4.911974000	1.639454000
C	1.105647000	-3.434714000	-1.583514000
C	-0.102051000	-2.014874000	-3.144125000
C	-0.356647000	4.273389000	-0.792170000
N	0.300870000	-4.920885000	0.246586000
C	-4.131316000	-3.038727000	2.324067000
C	-1.091519000	-6.591557000	0.681775000
C	-3.969951000	-5.763510000	2.016676000
C	1.842284000	-3.939405000	-2.659857000
C	1.375509000	-4.018931000	-0.213087000
C	0.665253000	-2.543056000	-4.186602000
C	-1.227940000	-1.070939000	-3.495073000
C	0.160699000	-6.266982000	0.171192000
C	-5.211570000	-3.824687000	2.726654000
H	-4.144165000	-1.957716000	2.421804000
H	-1.512586000	-7.580368000	0.776312000
H	-3.874319000	-6.834793000	1.881486000
C	-5.124455000	-5.207272000	2.568502000
H	2.588452000	-4.705045000	-2.458429000
C	1.662264000	-3.498180000	-3.974181000
H	2.293201000	-4.607723000	-0.226783000
H	1.470486000	-3.252430000	0.559492000
H	0.946969000	-6.888801000	-0.229854000
H	-6.092697000	-3.358176000	3.151364000
H	-5.945551000	-5.848955000	2.870527000
C	2.505071000	-4.029470000	-5.108299000
H	1.966746000	-3.983156000	-6.059444000
H	2.800903000	-5.068097000	-4.933381000
H	3.426037000	-3.444954000	-5.226418000
H	-0.303662000	4.896752000	-1.677155000
H	-0.522275000	1.924237000	2.235791000
C	-0.331050000	3.993700000	1.600694000

H	-0.262755000	4.389863000	2.606966000
H	0.460502000	-2.207750000	-5.201164000
C	-0.947980000	1.369918000	-4.227242000
H	-1.112483000	1.173718000	-5.276252000
H	-0.746343000	3.555356000	-3.960193000
C	-0.268055000	4.827636000	0.484789000
H	-0.147910000	5.899286000	0.603882000
H	-1.505952000	-1.190308000	-4.542337000
H	-2.109436000	-1.269599000	-2.879125000
H	2.154738000	0.806244000	-0.126453000
H	-1.391036000	-0.309998000	2.141144000
O	0.234471000	-2.433245000	2.725189000
P	0.693696000	-1.200142000	3.490241000
O	1.400008000	-1.679939000	4.893236000
C	2.755193000	-1.187324000	4.999052000
C	3.268548000	-1.043666000	3.558802000
O	2.091730000	-0.593958000	2.822571000
H	1.940519000	-0.181233000	1.050178000
H	2.747265000	-0.219318000	5.512731000
H	4.690135000	0.023805000	2.335488000
C	4.398633000	-0.050244000	3.386352000
H	5.270870000	-0.384343000	3.956993000
H	4.103637000	0.940200000	3.744727000
H	3.333477000	-1.908301000	5.578346000
H	3.549262000	-2.027158000	3.163144000

Table S11 Optimized-coordinates for $[Cu^{II}_2(L^1)(OH)(H_2O)(Cyp)]$ (**III^B**)

Cu	-0.352656000	0.089300000	-0.333870000
O	0.263265000	-0.029604000	1.575288000
O	1.808488000	0.835538000	-0.919677000
O	0.193202000	-1.768247000	-0.873653000
N	-0.968533000	2.066800000	0.015961000
N	-1.788700000	0.325313000	-1.725824000
C	-2.354652000	1.540140000	-1.822116000
Cu	-0.047028000	-3.416703000	0.357868000
C	0.448084000	-2.050023000	-2.172163000
O	-1.901551000	-2.989431000	0.494010000
C	-1.878455000	2.542031000	-0.866675000
C	-0.477001000	2.868826000	0.965879000
N	-2.389442000	-0.466544000	-2.616949000
C	-3.341865000	1.523868000	-2.821822000
N	1.774841000	-4.192888000	-0.207963000
N	-0.074072000	-5.300632000	1.317452000
C	2.056855000	-5.413691000	0.271752000
C	1.037428000	-6.046233000	1.111692000
C	1.763563000	-2.361957000	-2.590007000

C	-0.591537000	-2.095798000	-3.130743000
C	-2.315389000	3.865680000	-0.818685000
N	2.848083000	-3.787877000	-0.897211000
C	-1.043168000	-5.771768000	2.110690000
C	3.347289000	-5.805001000	-0.132262000
C	1.187543000	-7.307904000	1.691096000
C	2.022261000	-2.640535000	-3.933651000
C	2.865738000	-2.472970000	-1.566273000
C	-0.295735000	-2.377314000	-4.467222000
C	-2.021917000	-1.891205000	-2.693971000
C	3.815710000	-4.735517000	-0.880132000
C	-0.963651000	-7.018303000	2.727728000
H	-1.901123000	-5.125802000	2.261652000
H	3.870217000	-6.723385000	0.083966000
H	2.085631000	-7.886547000	1.508947000
C	0.171018000	-7.799111000	2.507196000
H	3.041871000	-2.874453000	-4.232348000
C	1.009879000	-2.635764000	-4.901667000
H	3.846827000	-2.387975000	-2.034522000
H	2.778250000	-1.711314000	-0.791799000
H	4.753526000	-4.581323000	-1.392573000
H	-1.772603000	-7.359421000	3.362873000
H	0.266869000	-8.776464000	2.968391000
C	1.316176000	-2.898931000	-6.356084000
H	0.447863000	-3.311076000	-6.877867000
H	2.148662000	-3.599708000	-6.468246000
H	1.598950000	-1.973613000	-6.873329000
H	-3.043287000	4.226473000	-1.536044000
H	0.234772000	2.411201000	1.643470000
C	-0.868389000	4.202232000	1.078062000
H	-0.451273000	4.823667000	1.861679000
H	-1.111111000	-2.411199000	-5.186682000
C	-3.331349000	0.220114000	-3.302367000
H	-3.925303000	-0.262231000	-4.064251000
H	-3.982487000	2.328750000	-3.146560000
C	-1.798585000	4.704742000	0.168187000
H	-2.122701000	5.738519000	0.225865000
H	-2.713341000	-2.341991000	-3.406576000
H	-2.185215000	-2.318893000	-1.697564000
H	1.935387000	1.783467000	-1.040454000
H	-2.439823000	-3.753299000	0.725727000
O	1.051530000	-2.422828000	2.151677000
P	1.332379000	-0.947379000	2.166167000
O	1.754561000	-0.454143000	3.667600000
C	2.969172000	0.332123000	3.636055000
C	3.782939000	-0.203098000	2.448463000
O	2.766511000	-0.523398000	1.445774000
H	2.341545000	0.580544000	-0.146068000
H	2.711562000	1.388325000	3.498400000
H	5.294843000	0.343180000	1.010307000
C	4.787742000	0.774866000	1.876840000
H	5.544829000	1.004036000	2.633202000

H	4.301706000	1.708667000	1.578443000
H	3.481135000	0.197268000	4.589450000
H	4.271979000	-1.144050000	2.725134000

Table S12 Optimized-coordinates for HPNP

O	-0.357254000	-0.043482000	1.954310000
O	-0.606817000	-2.591548000	2.601795000
P	-0.004796000	-1.231313000	2.801858000
O	1.617105000	-1.441938000	2.890616000
O	-0.350385000	-0.694304000	4.380389000
C	-0.222547000	-1.378722000	5.540396000
C	-0.637475000	-0.699209000	6.702430000
C	0.295564000	-2.684337000	5.634749000
C	-0.536299000	-1.305901000	7.941934000
H	-1.034417000	0.305198000	6.607004000
C	0.398247000	-3.294959000	6.876510000
H	0.602505000	-3.211441000	4.741352000
C	-0.015968000	-2.605389000	8.021825000
H	-0.851854000	-0.790752000	8.840216000
H	0.794959000	-4.298533000	6.964121000
N	0.094038000	-3.248171000	9.317020000
O	-0.273565000	-2.627692000	10.318468000
O	0.551336000	-4.392908000	9.373752000
C	2.509905000	-0.319278000	2.992019000
C	3.947615000	-0.802311000	2.818681000
O	4.165135000	-1.360415000	1.514772000
H	4.087524000	-0.658192000	0.856825000
H	2.260420000	0.423812000	2.225215000
H	5.964923000	-0.041719000	2.982326000
C	4.942442000	0.318799000	3.121368000
H	4.838043000	0.667305000	4.153407000
H	4.785430000	1.176008000	2.456090000
H	2.398157000	0.148773000	3.977624000
H	4.114715000	-1.640466000	3.503043000

Table S13 Optimized-coordinates for Cyp

O	0.004926000	0.002228000	-0.012146000
O	-0.023114000	0.021517000	2.594929000
P	0.751254000	-0.015764000	1.299768000
O	1.928533000	1.172448000	1.346108000
C	3.227662000	0.621332000	1.077025000
C	3.184675000	-0.822718000	1.598725000
O	1.847668000	-1.274859000	1.278226000
H	3.423201000	0.639463000	-0.003357000
H	4.102055000	-2.764120000	1.372370000
C	4.210976000	-1.750280000	0.977857000
H	5.221276000	-1.400806000	1.214755000

H	4.098119000	-1.782255000	-0.110067000
H	3.976529000	1.228396000	1.590379000
H	3.289936000	-0.816964000	2.692427000

Table S14 Optimized-coordinates for PNP (*p*-nitro-phenol)

O	-0.004529000	-0.101995000	0.012720000
C	0.000379000	-0.021660000	1.276404000
C	1.231563000	0.017497000	2.042552000
C	-1.224891000	0.036889000	2.050758000
C	1.235979000	0.103868000	3.410291000
H	2.167457000	-0.024018000	1.492372000
C	-1.218929000	0.123979000	3.418441000
H	-2.164913000	0.009256000	1.506761000
C	0.011264000	0.158931000	4.125545000
H	2.168059000	0.131681000	3.962676000
H	-2.146808000	0.166240000	3.976953000
N	0.016791000	0.248833000	5.525869000
O	1.109296000	0.274065000	6.143752000
O	-1.070721000	0.303590000	6.150639000

Table S15 Optimized-coordinates for $[Cu^{II}_2(L^1)(\mu\text{-OMe})(OMe)(HPNP)]$

Cu	-0.787753000	0.174927000	0.042621000
O	-0.366287000	0.529232000	4.380118000
O	1.001888000	0.884050000	-0.178660000
O	-0.275462000	-1.805744000	-0.260706000
N	-1.741811000	2.081468000	-0.043746000
N	-1.740696000	0.230640000	-1.972786000
C	-2.041773000	1.478810000	-2.343012000
Cu	-1.062015000	-2.449556000	1.521726000
C	0.499701000	-2.332387000	-1.210360000
O	-2.101140000	-0.846632000	1.203381000
C	-2.183421000	2.469493000	-1.265624000
C	-1.836246000	2.927411000	0.989455000
N	-1.596702000	-0.482856000	-3.088388000
C	-2.115377000	1.562434000	-3.752828000
N	0.098549000	-4.072316000	1.501119000
N	-2.456118000	-4.104557000	2.148487000
C	-0.381171000	-5.246458000	1.929693000
C	-1.799101000	-5.277852000	2.310092000
C	1.739427000	-2.950806000	-0.894811000
C	0.095259000	-2.310745000	-2.575931000
C	-2.732576000	3.739398000	-1.467190000
N	1.384948000	-4.247077000	1.182652000
C	-3.759253000	-4.048212000	2.440029000
C	0.642124000	-6.214640000	1.884802000
C	-2.440736000	-6.424139000	2.784126000
C	2.569996000	-3.422381000	-1.914514000

C	2.146316000	-3.149658000	0.548494000
C	0.962761000	-2.789348000	-3.563234000
C	-1.314837000	-1.923860000	-2.981566000
C	1.749434000	-5.534811000	1.395586000
C	-4.474817000	-5.147560000	2.915011000
H	-4.245587000	-3.090454000	2.285167000
H	0.593924000	-7.255947000	2.162666000
H	-1.887895000	-7.348611000	2.906522000
C	-3.798223000	-6.353838000	3.092789000
H	3.519822000	-3.879050000	-1.643185000
C	2.220615000	-3.326174000	-3.266330000
H	3.196836000	-3.434258000	0.616624000
H	1.998794000	-2.250434000	1.148617000
H	2.754373000	-5.869865000	1.185858000
H	-5.531251000	-5.052235000	3.137709000
H	-4.319293000	-7.230329000	3.463730000
C	3.154097000	-3.794249000	-4.357019000
H	2.600027000	-4.138248000	-5.235592000
H	3.791493000	-4.614374000	-4.013206000
H	3.817275000	-2.985159000	-4.688334000
H	-3.086167000	4.025190000	-2.451338000
H	-1.461898000	2.565433000	1.941688000
C	-2.371860000	4.207307000	0.864554000
H	-2.425769000	4.859293000	1.728604000
H	0.631317000	-2.766449000	-4.599650000
C	-1.821843000	0.279498000	-4.191158000
H	-1.763000000	-0.137857000	-5.185539000
H	-2.334519000	2.421929000	-4.367757000
C	-2.824780000	4.617391000	-0.389892000
H	-3.247935000	5.607034000	-0.527898000
H	-1.539971000	-2.348549000	-3.961025000
H	-2.035397000	-2.320597000	-2.261653000
O	-0.480457000	-1.974938000	3.546830000
P	0.282270000	-0.790537000	4.105158000
O	1.625021000	-0.647342000	3.197941000
O	0.909536000	-1.254689000	5.599226000
C	1.598937000	-2.377941000	5.920431000
C	2.094083000	-2.433326000	7.236356000
C	1.827981000	-3.444420000	5.032360000
C	2.814097000	-3.535120000	7.665600000
H	1.904022000	-1.599984000	7.903242000
C	2.550564000	-4.549948000	5.460126000
H	1.427389000	-3.409017000	4.028407000
C	3.039959000	-4.589181000	6.770166000
H	3.201343000	-3.586683000	8.675150000
H	2.732157000	-5.379542000	4.788595000
N	3.795460000	-5.747662000	7.212017000
O	4.212736000	-5.772922000	8.372344000
O	3.993239000	-6.664956000	6.411604000
C	2.330649000	0.609961000	3.106870000
C	3.552389000	0.438801000	2.206695000
O	3.216734000	-0.060555000	0.921002000

H	2.365952000	0.330401000	0.574373000
H	1.654668000	1.365957000	2.694603000
H	5.205247000	1.635914000	1.490543000
C	4.320711000	1.763271000	2.120533000
H	4.650701000	2.100162000	3.109320000
H	3.696617000	2.548281000	1.678765000
H	2.650808000	0.929355000	4.105007000
H	4.204539000	-0.318724000	2.661905000
C	-2.970868000	-0.255301000	2.146880000
H	-2.427466000	0.290548000	2.927290000
H	-3.652451000	0.436213000	1.632584000
H	-3.589283000	-1.020027000	2.636114000
C	1.275952000	1.995850000	-0.989357000
H	0.912401000	1.866294000	-2.022399000
H	0.840740000	2.930608000	-0.599658000
H	2.365749000	2.147270000	-1.051258000

Table S16 Optimized-coordinates for $[Cu^{II}_2(L^1)(\mu\text{-OMe})(OMe)(HPNP)]^{\#}$

Cu	-2.621463000	-0.786327000	-0.420700000
O	0.961812000	-3.213814000	1.216318000
O	-2.358579000	-1.025255000	1.725065000
O	-1.818528000	1.060794000	-0.349606000
N	-3.602954000	-2.618798000	-0.599262000
N	-4.430822000	-0.207507000	-1.157082000
C	-5.338656000	-1.176791000	-1.335915000
Cu	0.169229000	0.321980000	-0.468311000
C	-2.439928000	2.108965000	0.215169000
O	-0.836847000	-1.084954000	-1.312557000
C	-4.901624000	-2.530983000	-0.980960000
C	-3.087328000	-3.807823000	-0.267756000
N	-4.960086000	0.927996000	-1.611640000
C	-6.504814000	-0.633326000	-1.908839000
N	0.874234000	2.067885000	0.202178000
N	1.661875000	1.220635000	-2.199648000
C	1.832629000	2.775637000	-0.409079000
C	2.348312000	2.264558000	-1.687274000
C	-1.957965000	2.728591000	1.400475000
C	-3.612395000	2.649884000	-0.381069000
C	-5.718322000	-3.660939000	-1.039397000
N	0.512781000	2.737393000	1.302025000
C	2.060838000	0.702710000	-3.364101000
C	2.103082000	3.939121000	0.341500000
C	3.457044000	2.818640000	-2.334492000
C	-2.657494000	3.798712000	1.964951000
C	-0.669687000	2.279216000	2.052004000
C	-4.283633000	3.716951000	0.222397000
C	-4.117768000	2.135023000	-1.707941000

C	1.230494000	3.880091000	1.418443000
C	3.154471000	1.193209000	-4.080656000
H	1.480682000	-0.136072000	-3.739040000
H	2.817594000	4.719565000	0.130877000
H	3.990964000	3.652832000	-1.893041000
C	3.863005000	2.271543000	-3.550840000
H	-2.265347000	4.250305000	2.873927000
C	-3.837897000	4.304944000	1.409804000
H	-0.584763000	2.692979000	3.057501000
H	-0.590131000	1.189979000	2.108162000
H	1.067252000	4.559486000	2.241750000
H	3.436454000	0.739301000	-5.024011000
H	4.720525000	2.681492000	-4.074632000
C	-4.596244000	5.433508000	2.065401000
H	-5.316286000	5.053172000	2.800798000
H	-5.159949000	6.014656000	1.329808000
H	-3.921782000	6.113246000	2.594406000
H	-6.754407000	-3.567754000	-1.343590000
H	-2.046189000	-3.811760000	0.036907000
C	-3.840394000	-4.979616000	-0.308246000
H	-3.384601000	-5.924426000	-0.036706000
H	-5.174373000	4.111041000	-0.262267000
C	-6.216259000	0.714634000	-2.074908000
H	-6.799937000	1.520898000	-2.493278000
H	-7.419283000	-1.137450000	-2.179950000
C	-5.176979000	-4.899963000	-0.699419000
H	-5.793810000	-5.791593000	-0.738531000
H	-4.734635000	2.889685000	-2.196776000
H	-3.284285000	1.883841000	-2.369679000
O	1.683670000	-0.811298000	0.208723000
P	1.767246000	-1.944309000	1.243963000
O	2.536145000	-1.569084000	2.650621000
O	3.296593000	-2.646964000	0.611970000
C	4.427963000	-2.031885000	0.293798000
C	5.398806000	-2.803360000	-0.394983000
C	4.727718000	-0.682085000	0.606895000
C	6.612698000	-2.257832000	-0.762491000
H	5.164048000	-3.836191000	-0.628959000
C	5.943760000	-0.133231000	0.239627000
H	3.999946000	-0.082971000	1.135701000
C	6.886053000	-0.915936000	-0.445940000
H	7.350130000	-2.849138000	-1.290752000
H	6.175843000	0.897104000	0.479349000
N	8.145384000	-0.337302000	-0.829513000
O	8.967125000	-1.038845000	-1.435297000
O	8.373746000	0.846257000	-0.544435000
C	1.776107000	-1.475828000	3.864814000
C	0.592401000	-0.539122000	3.618692000
O	0.085177000	-0.888931000	2.366513000
H	-1.376384000	-0.999078000	2.047733000
H	1.424331000	-2.476981000	4.147276000
H	-1.259587000	0.061905000	4.587233000

C	-0.426138000	-0.626657000	4.758985000
H	0.033496000	-0.363053000	5.719207000
H	-0.830896000	-1.641919000	4.837955000
H	2.465873000	-1.108678000	4.629392000
H	0.995238000	0.495178000	3.602797000
C	-0.298791000	-2.273448000	-1.851018000
H	0.045590000	-2.962178000	-1.070876000
H	-1.062356000	-2.773466000	-2.463252000
H	0.552268000	-2.044707000	-2.507267000
C	-3.164238000	-1.823106000	2.584023000
H	-4.198279000	-1.779918000	2.231503000
H	-2.841566000	-2.872562000	2.590521000
H	-3.133384000	-1.442186000	3.611405000