

Electronic Supplementary Information for

Understanding the factors in the catalytic nitrite reduction cycle by bio-inspired copper(II) complexes

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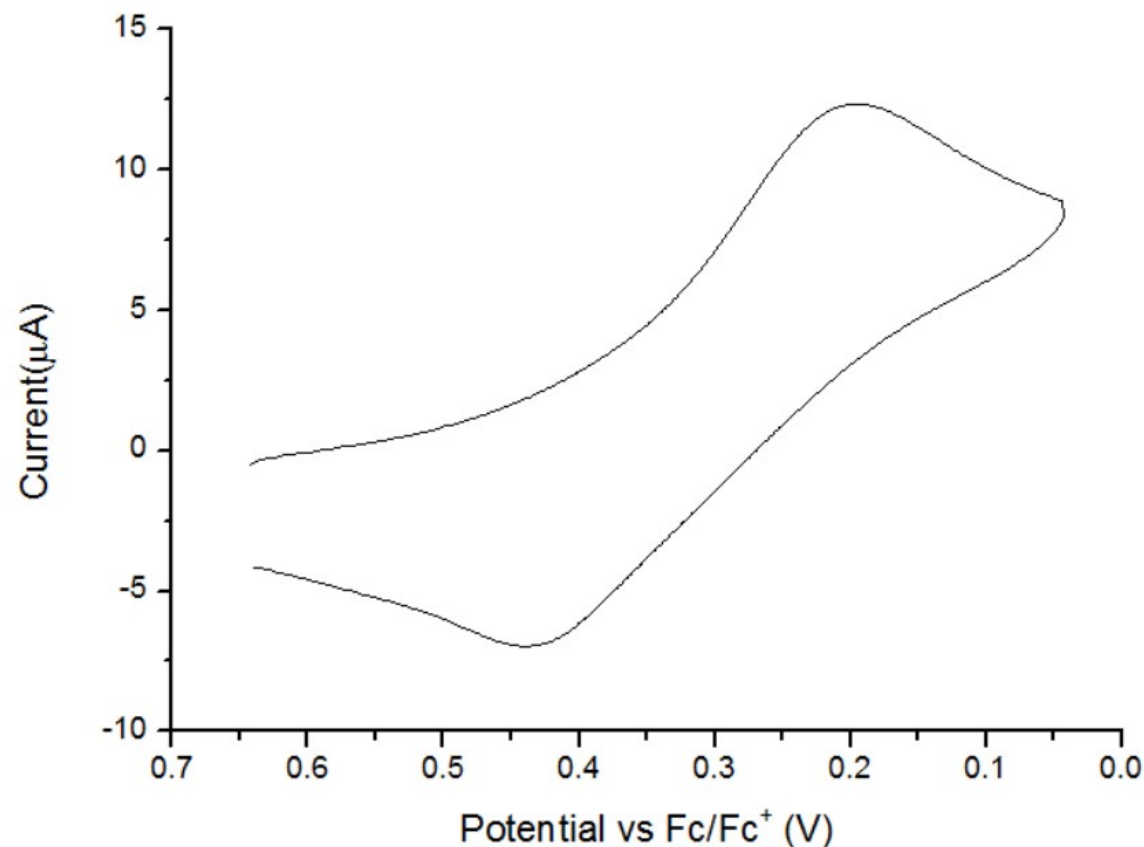


Figure S1. Cyclic voltammetry of $\text{Me}_2\text{TpmCu}^{\text{II}}(\text{NO}_3)_2$ where the measured reduction peak is 0.20 V and $E_{1/2}$ is 0.32 V vs. Fc and the. Cyclic voltammetry measurements were taken in 10^{-4} M CH_3OH solutions using 0.1 M $(\text{Bu}_4\text{N})(\text{PF}_6)$ as supporting electrolyte and referenced to $\text{Fc}^{+/0}$.

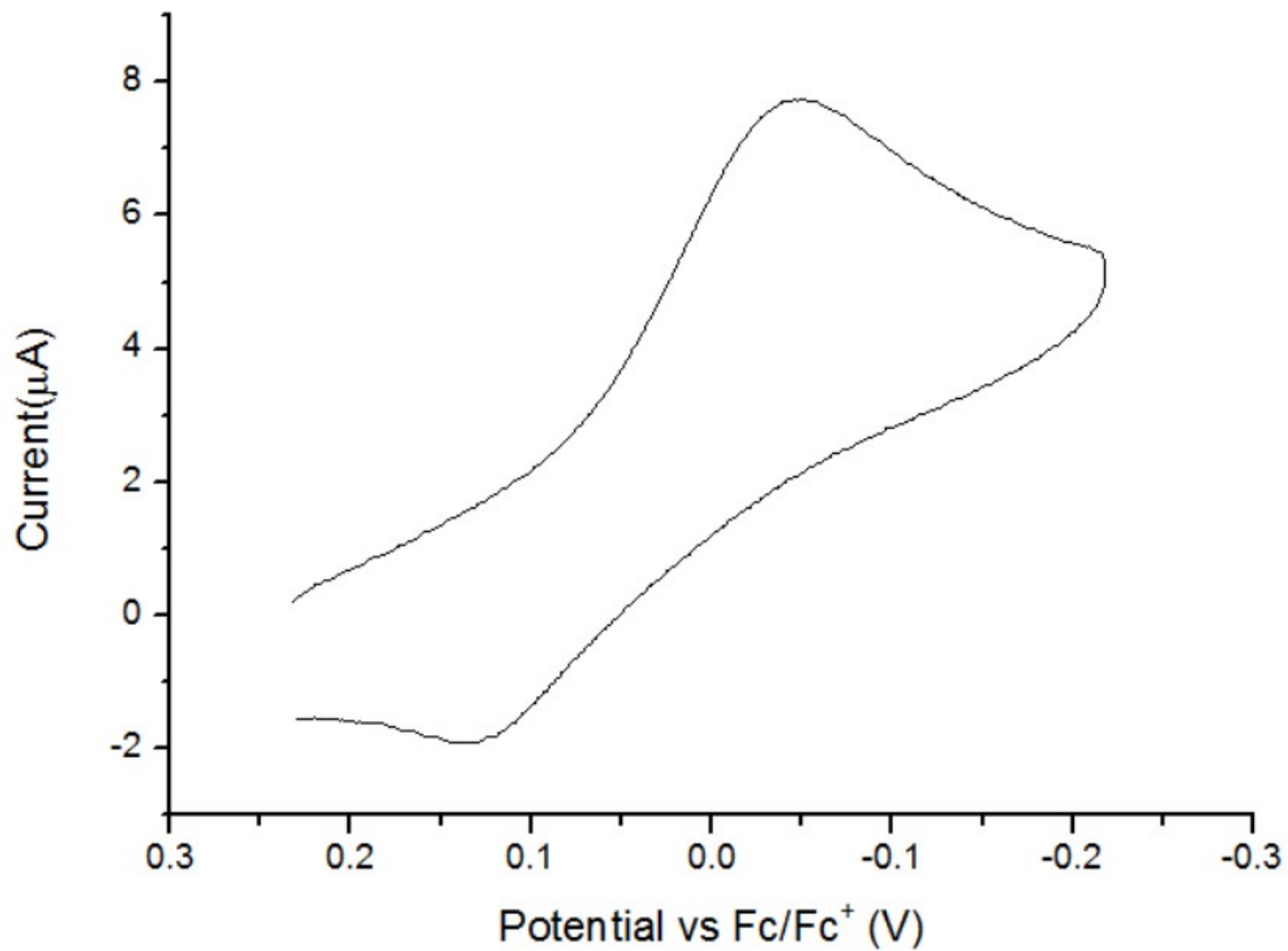


Figure S2. Cyclic voltammetry of $\text{Me}^2\text{TpCu}^{\text{II}}\text{NO}_3$ where the measured reduction peak is -0.05 V and $E_{1/2}$ is 0.04 V vs. Fc. Cyclic voltammetry measurements were taken in 10^{-4} M CH_3OH solutions using 0.1 M $(\text{Bu}_4\text{N})(\text{PF}_6)$ as supporting electrolyte and referenced to $\text{Fc}^{+/0}$.

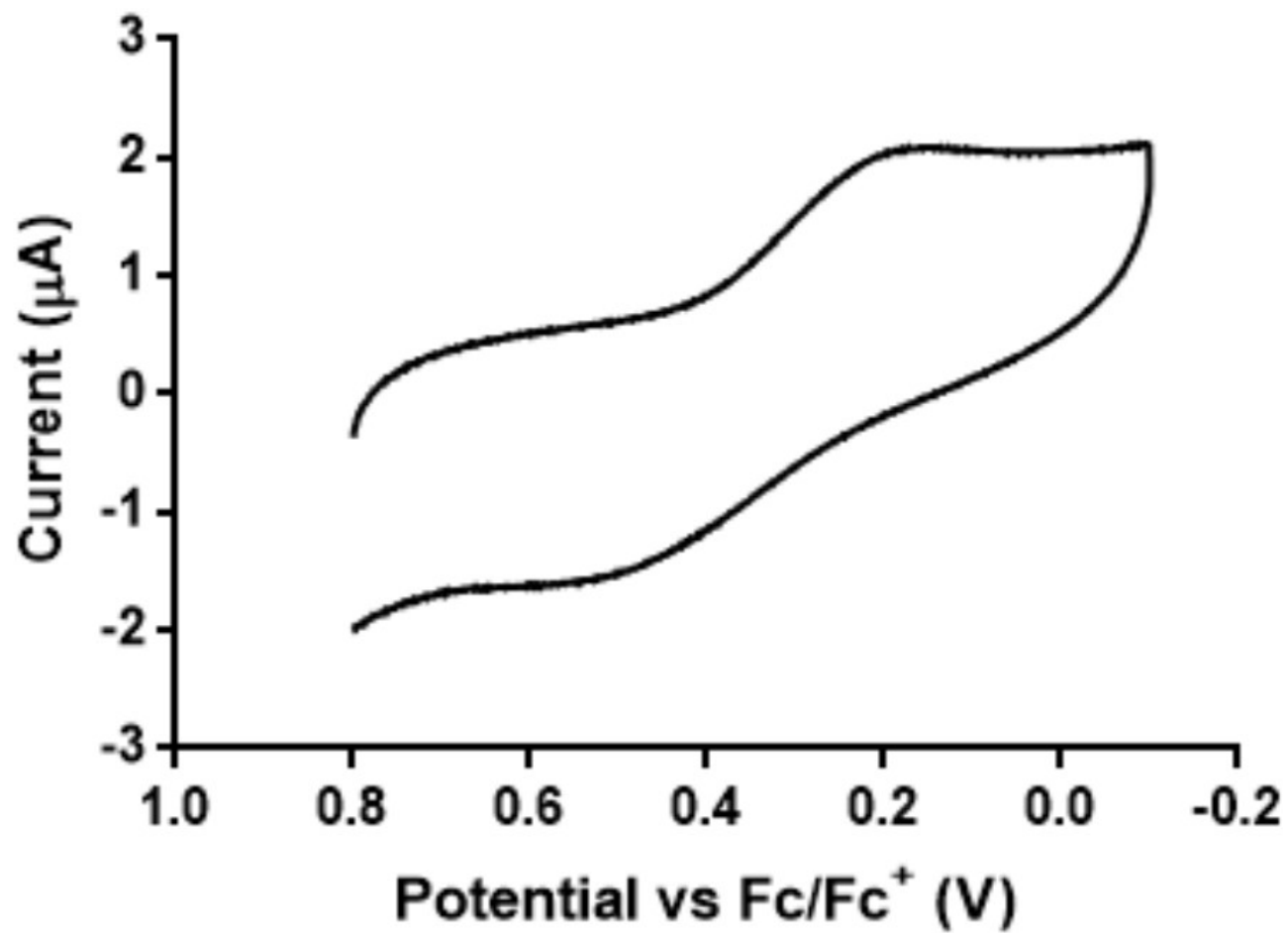


Figure S3. Cyclic voltammetry of $i\text{PrTICCu}^{\text{II}}(\text{NO}_3)_2$ where the measured reduction peak is 0.17 V and $E_{1/2}$ is 0.32 V vs. Fc. Cyclic voltammetry measurements were taken in 10^{-4} M CH_3OH solutions using 0.1 M $(\text{Bu}_4\text{N})(\text{PF}_6)$ as supporting electrolyte and referenced to $\text{Fc}^{+/0}$.

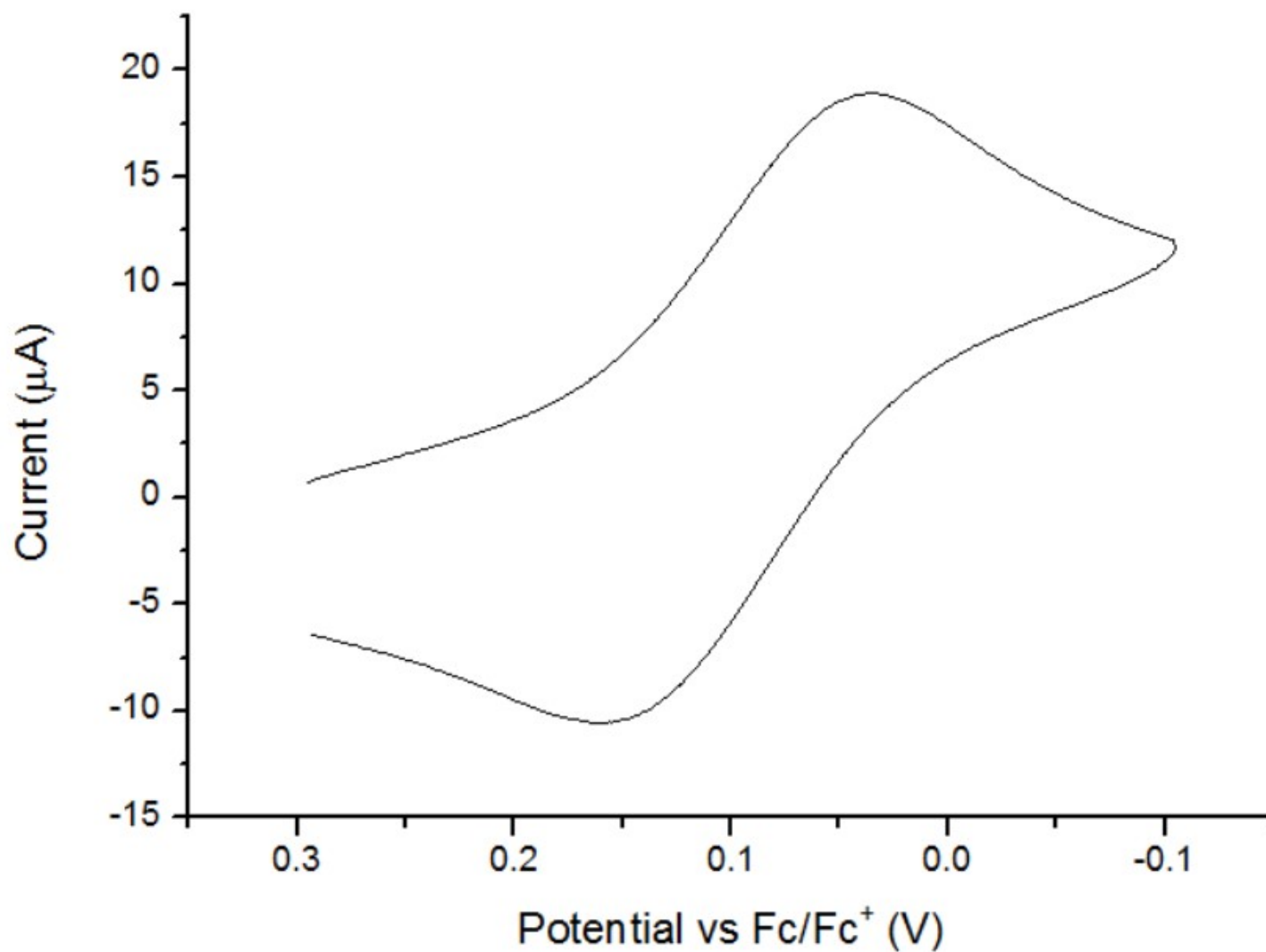


Figure S4. Cyclic voltammetry of $\text{Cu}^{\text{II}}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ salt where the measured reduction peak is 0.04 V and $E_{1/2}$ is 0.095 V vs. Fc. Cyclic voltammetry measurements were taken in 10^{-4} M CH_3OH solutions using 0.1 M $(\text{Bu}_4\text{N})(\text{PF}_6)$ as supporting electrolyte and referenced to $\text{Fc}^{+/0}$.

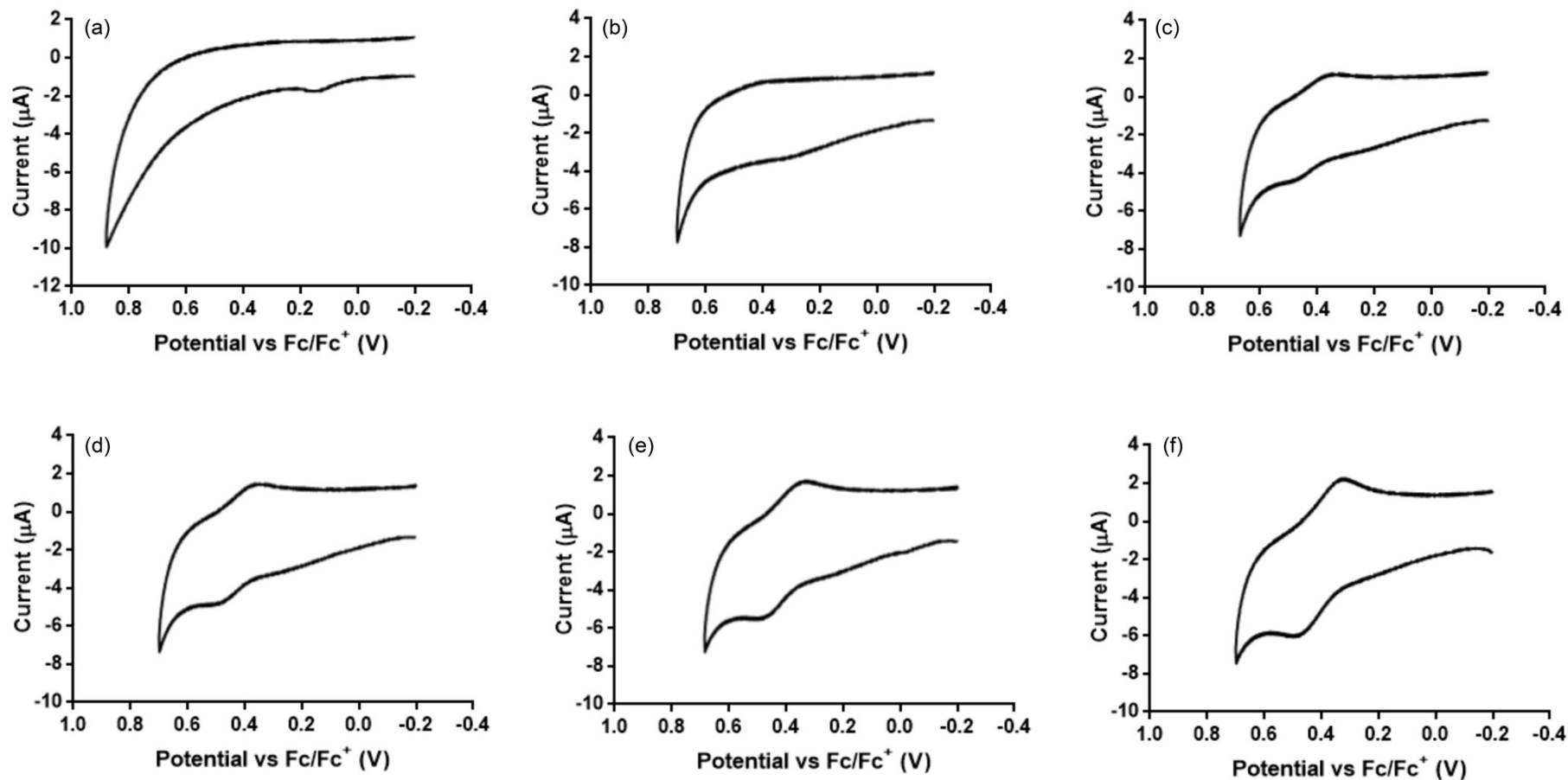


Figure S5. (a) Cyclic voltammetry of ascorbic acid where the measured oxidation peak is 0.15 V vs. Fc. (b)-(f) Ascorbic acid with diifrernt equivalents HCl from 0.05, 0.10, 0.15, 0.25, to 0.50. Cyclic voltammetry measurements were taken in 10^{-4} M CH_3OH solutions using 0.1 M $(\text{Bu}_4\text{N})(\text{PF}_6)$ as supporting electrolyte and referenced to $\text{Fc}^{+/0}$.

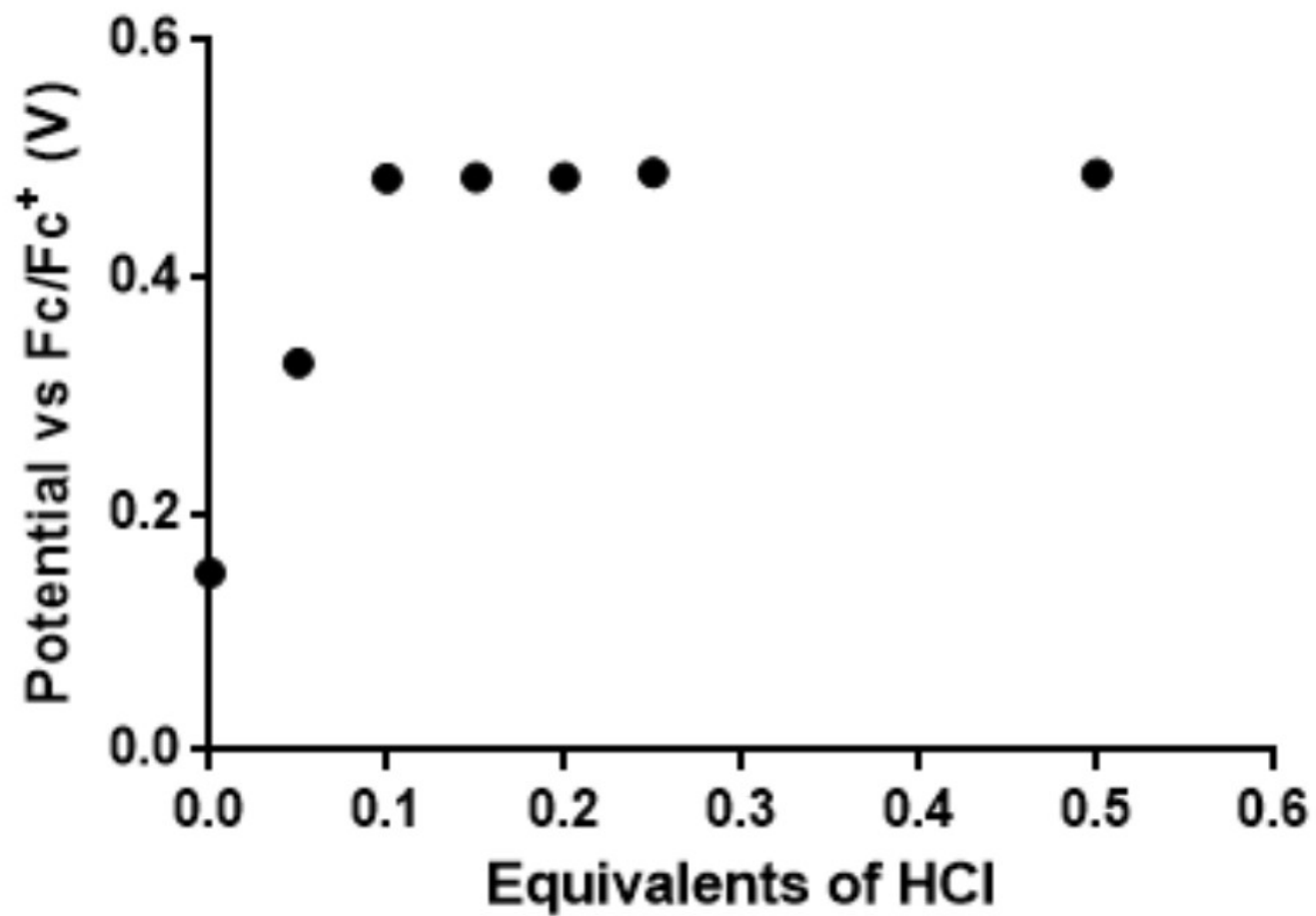


Figure S6. Oxidation peak of ascorbic acid with different equivalents HCl from 0.05, 0.10, 0.15, 0.25, to 0.50. Cyclic voltammetry measurements were taken in 10^{-4} M CH₃OH solutions using 0.1 M (Bu₄N)(PF₆) as supporting electrolyte and referenced to Fc⁺⁰.

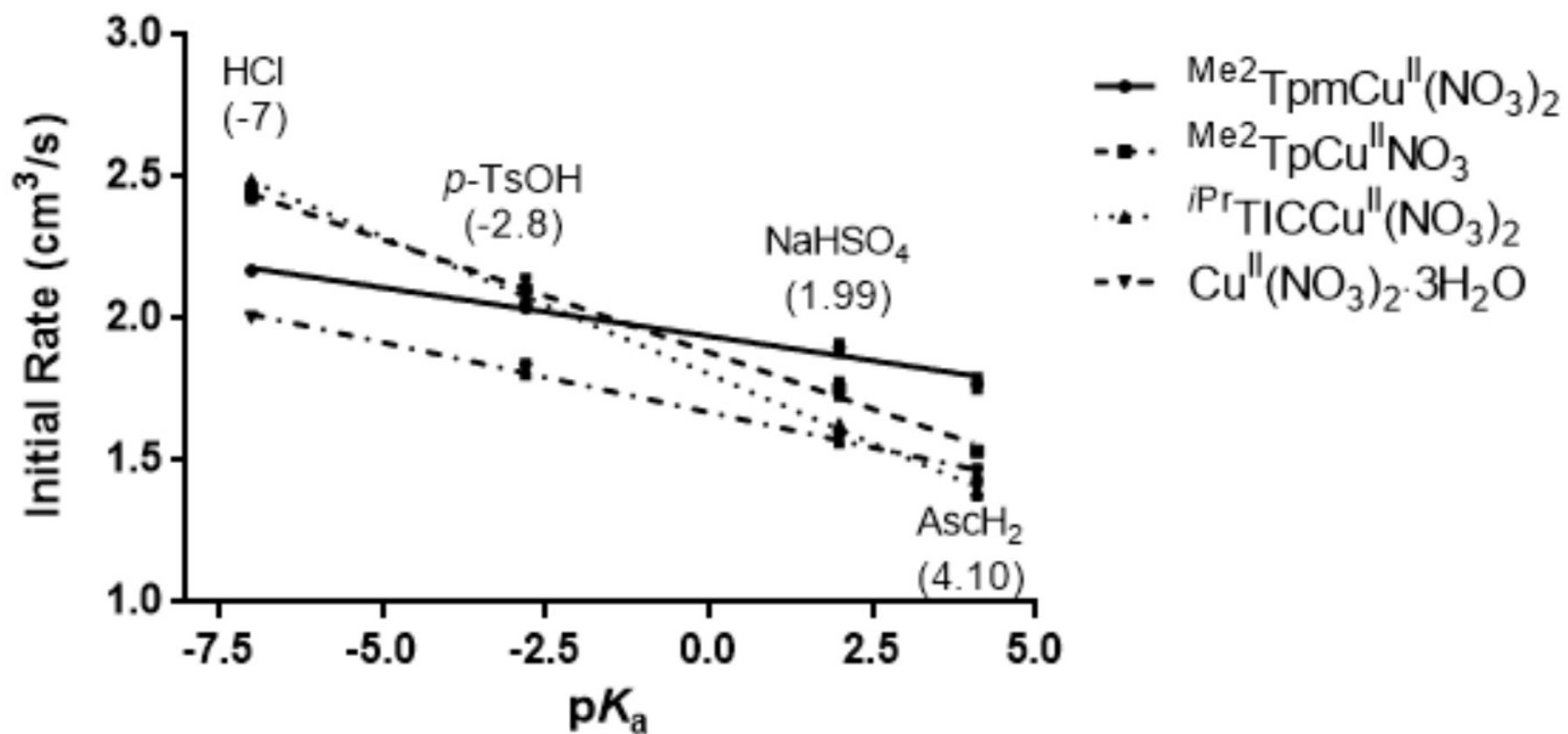


Figure S7. Initial rates with four different acids [(HCl, pK_a ~ -7 in H₂O), (*p*-TsOH, pK_a ~ -2.8 in H₂O), (NaHSO₄, pK_a ~ 1.99 in H₂O), and (AsCH₂, pK_{a1} ~ 4.2 in H₂O)] in catalytic cycles involving Me²TpmCu^{II}(NO₃)₂ (solid line), Me²TpCu^{II}NO₃ (dash line), *i*PrTICCu^{II}(NO₃)₂ (dot line), and Cu^{II}(NO₃)₂·3H₂O (dash-dot line).

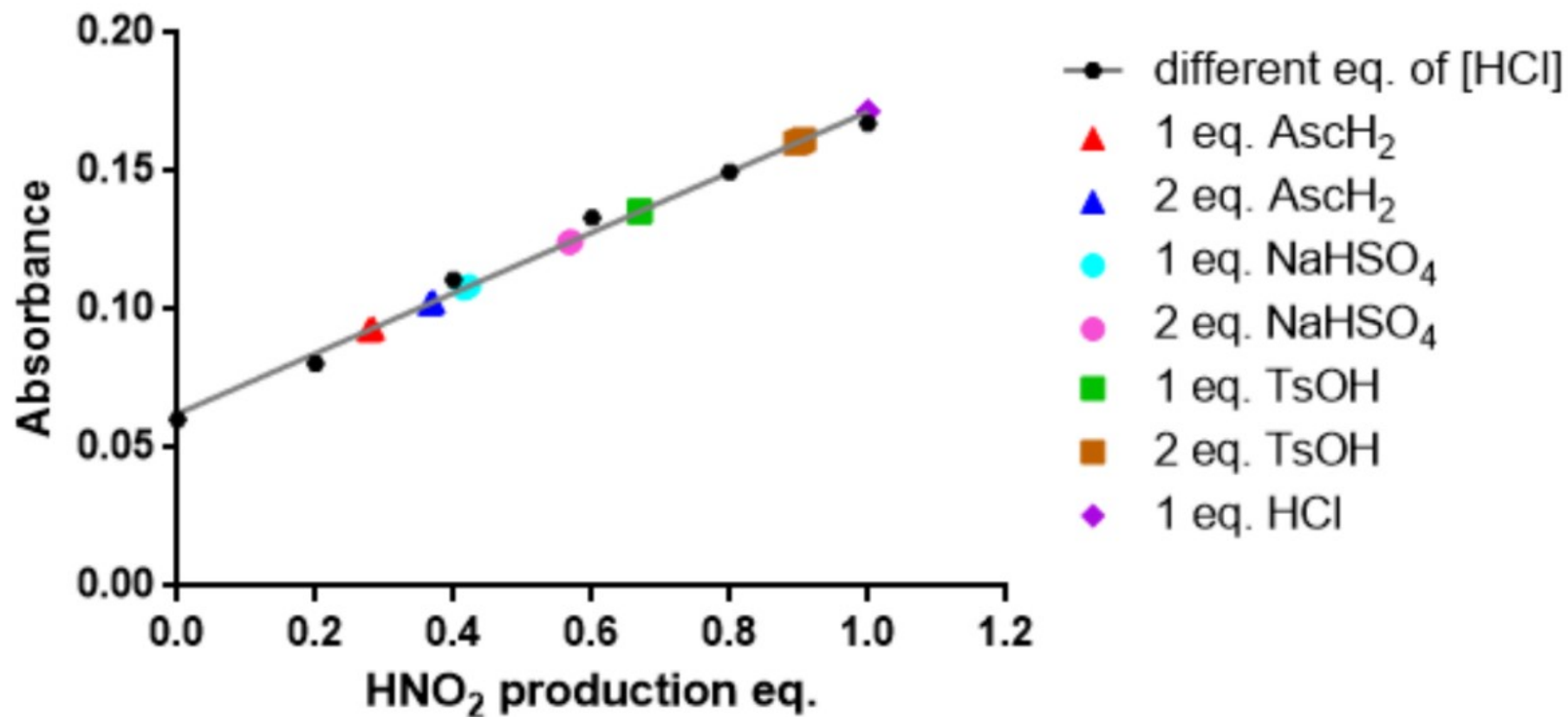


Figure S8. HNO₂ generation experiments of ascorbic acid as proton source. The HNO₂ amounts were performed by calibrating curve response with known equivalents of HCl mixed with nitrite anion (0.2, 0.4, 0.6, 0.8, and 1.0 of HCl).

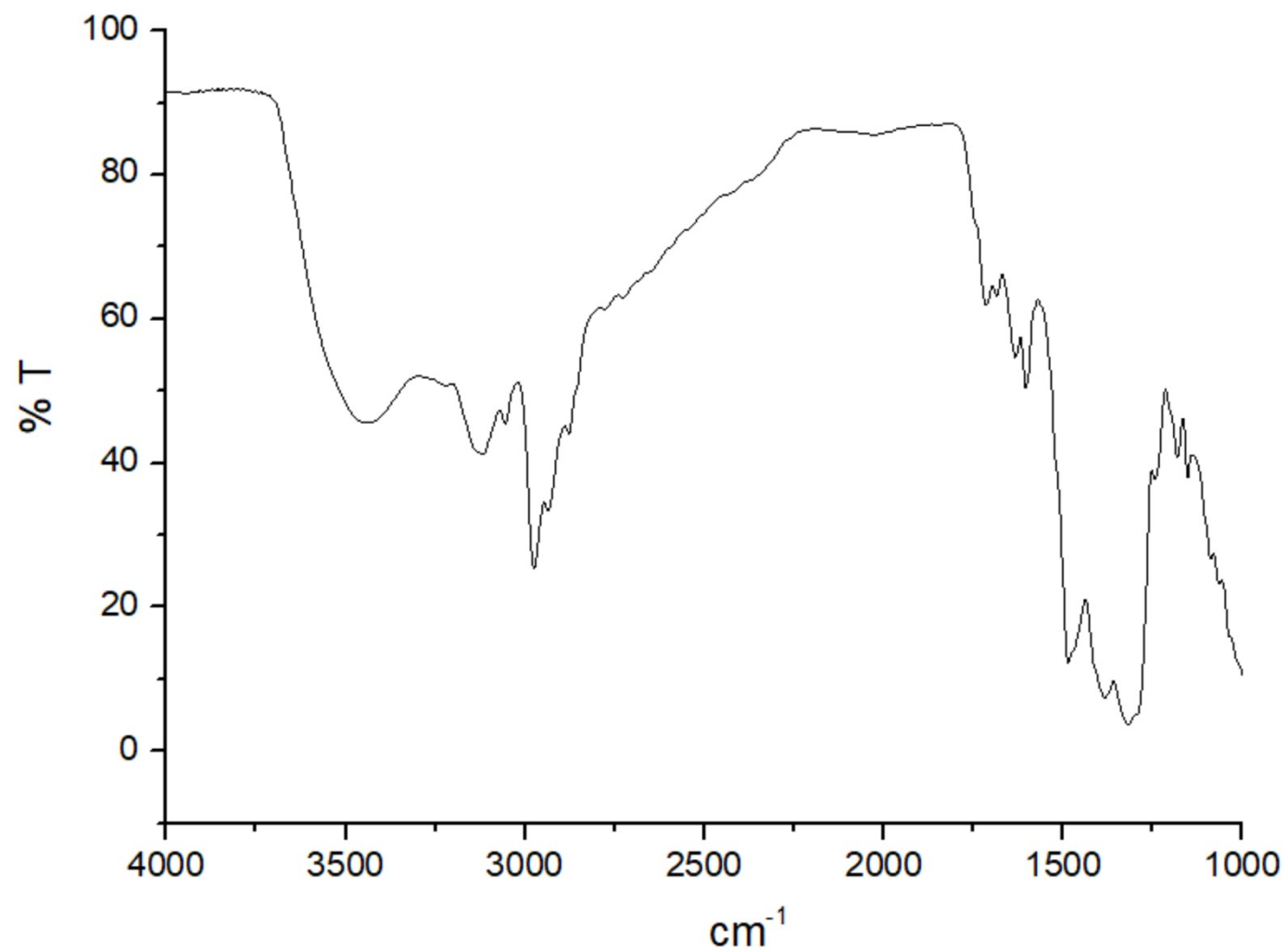


Figure S9. IR spectrum of $iPrTICCu(NO_3)_2$ complex.

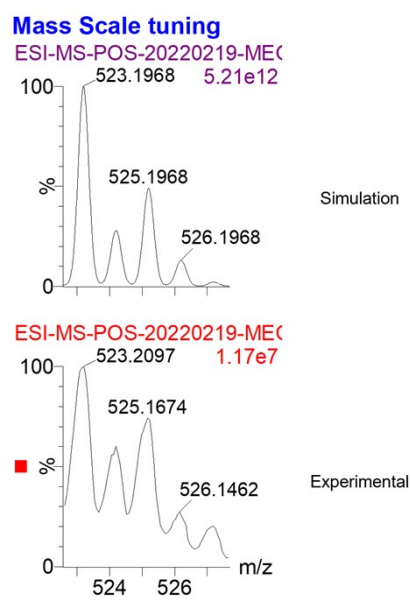


Figure S10. ESI-MS spectrum of $i\text{PrTICCu}^{\text{II}}(\text{NO}_3)_2$; $m/z = 523.2097$ ($[i\text{PrTICCuNO}_3]^+$)

Table S1. Experimental catalytic reduction of nitrite anions by Cu^{II} complexes with proton sources exhibiting different pK_a .^[a]

Entry	Acid ^[b]	NO generation rate ^[c]			
		$\text{Me}_2\text{TpmCu}^{\text{II}}(\text{NO}_3)_2$	$\text{Me}_2\text{TpCu}^{\text{II}}\text{NO}_3$	$i\text{PrTICCu}^{\text{II}}(\text{NO}_3)_2$	$\text{Cu}^{\text{II}}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$
1	hydrochloric acid	2.17±0.02	2.44±0.02	2.49±0.03	2.01±0.02
2	<i>p</i> -Toluenesulfonic acid	2.04±0.01	2.10±0.05	2.07±0.03	1.82±0.03
3	Sodium hydrogen sulfate	1.90±0.02	1.75±0.03	1.63±0.02	1.58±0.02
4	Ascorbic acid	1.77±0.03	1.53±0.02	1.40±0.03	1.46±0.02

^[a]General conditions: copper complex (0.04 mmol), sodium nitrite (4.09 mmol), and ascorbic acid (8.18 mmol) in 40 mL CH_3OH . ^[b]Ascorbic acid (4.09 mmol) with a second acid (4.09 mmol) ^[c]Initial NO_2^- conversion rate ($\text{cm}^3 \text{s}^{-1}$).

Table S2. M06/6-31+G* relative free energies (kcal/mol) of different binding modes

	κ^1-N	κ^1-O	$\kappa^1-O(H)$
Me ² TpmCu ^I (HNO ₂)	0.0	4.9	5.2
Me ² TpCu ^I (HNO ₂)	0.0	5.9	6.1
<i>i</i> PrTICCu ^I (HNO ₂)	0.0	0.7	2.3

DFT optimized xyz coordinates

Me²TpmCu^I(H₂O)

Cu	-2.09465600	13.93838500	3.92247500
N	-0.82331500	15.61123000	4.21842500
N	0.49363200	15.31400800	4.03294400
N	-0.87820200	13.38967500	2.27635000
N	0.45264000	13.41813500	2.57062800
N	-0.78907600	12.81466900	5.16979600
N	0.52487200	13.10022200	4.94456800
C	-2.17944600	17.62143700	4.53793400
C	-0.88038400	16.93506100	4.32427000
C	0.41008100	17.49475700	4.20095900
C	1.27210000	16.43656400	4.00822700
C	2.73929200	16.40346200	3.79508500
C	-2.28789800	12.64565000	0.42039900
C	-0.96702300	12.83597600	1.07118900
C	0.31654000	12.50317600	0.58663200
C	1.20884900	12.88160300	1.56658200
C	2.68681000	12.77063000	1.62957800
C	-2.09679900	11.60014300	6.84371900
C	-0.81288300	12.10134600	6.29120600
C	0.49499400	11.93391500	6.79677200
C	1.33287300	12.59215500	5.92254400
C	2.80229500	12.79247100	5.94838700
C	0.91103400	13.94393500	3.83669100
H	2.00487200	13.94523000	3.80358600
H	-2.99454600	16.88803000	4.59213600
H	0.68121800	18.54407300	4.24763300
H	3.24921900	15.77993400	4.54215900
H	-3.09318900	12.99792500	1.07797300
H	0.56353900	12.04323300	-0.36429100
H	3.16568000	13.74677200	1.79015100
H	-2.94163000	11.96552700	6.24570300
H	0.79225400	11.39790300	7.69183400
H	3.06309600	13.85424500	6.06438200
H	-2.34735400	13.19951600	-0.52572100
H	-2.46794300	11.58764800	0.18973000
H	3.06267800	12.36276100	0.68549400
H	3.00963700	12.10038700	2.43828800
H	-2.39735600	18.32144700	3.72081100
H	-2.17389900	18.20139100	5.47000100

H	-2.12555700	10.50241700	6.84778300
H	-2.23794400	11.93255700	7.88013600
H	3.28657500	12.42608000	5.03276800
H	3.23016000	12.24737500	6.79618100
H	3.14343600	17.41827100	3.87098000
H	2.99572700	16.01110700	2.80090900
O	-4.14149100	13.95411700	4.12651700
H	-4.53920100	14.49408500	3.42340600
H	-4.49043300	13.06038500	3.97354100

Me²TpmCu^{II}(H₂O)

Cu	-1.59570400	14.58483700	4.67074900
N	-0.32387500	16.28170500	4.84781400
N	0.99022900	15.99810200	4.61554000
N	-0.45146900	13.91092400	3.02836600
N	0.89248300	14.07729600	3.18760800
N	-0.32274800	13.64156100	5.81280000
N	1.00185600	13.81112300	5.54554700
C	-1.69679400	18.28251200	5.21690100
C	-0.40089700	17.60481100	4.96359800
C	0.87640800	18.17614600	4.80037500
C	1.74885500	17.13155600	4.57628900
C	3.21115600	17.12324600	4.33761700
C	-1.96715100	13.02488400	1.30864200
C	-0.61651800	13.34956500	1.83250200
C	0.63637300	13.15550600	1.21858700
C	1.58521700	13.62285400	2.10391100
C	3.06261100	13.66768400	2.00918800
C	-1.71750800	12.45395600	7.44845800
C	-0.40775500	12.84424000	6.87614100
C	0.88795500	12.49471300	7.29534000
C	1.76827600	13.11954800	6.43551800
C	3.24797600	13.11033500	6.39159500
C	1.40474100	14.62764900	4.42240600
H	2.49799300	14.61022100	4.36794600
H	-2.41005500	17.60418900	5.70009000
H	1.13377000	19.22849700	4.84879000
H	3.74878200	16.57266200	5.12130500
H	-2.69913900	12.94747100	2.12093900
H	0.82675800	12.71639100	0.24546800
H	3.44363300	14.69594600	2.06898900

H	-2.54411500	12.81676400	6.82628500	C	-0.88831200	12.30615900	6.27910400
H	1.15092600	11.85659800	8.13130800	C	0.40086600	11.96279800	6.73652000
H	3.66266400	14.11921800	6.51869600	C	1.29264900	12.59279500	5.89444300
H	-2.31278800	13.79720400	0.60820600	C	2.77490600	12.60590700	5.88347500
H	-1.95002100	12.07474200	0.76213100	C	0.97508000	14.07915000	3.87281400
H	3.37845000	13.24505900	1.05006700	H	2.06889000	14.03286400	3.84842700
H	3.53848400	13.08409500	2.80878100	H	-2.84369800	17.19751400	4.38266800
H	-2.14311100	18.63935400	4.27858700	H	0.90403900	18.69142600	4.17467500
H	-1.55545200	19.15642700	5.86319400	H	3.36525800	15.87968200	4.64016400
H	-1.79498400	11.36294400	7.52848200	H	-3.03894500	13.46555500	0.99744700
H	-1.83839000	12.86535400	8.45858500	H	0.51838400	12.12048200	-0.29587600
H	3.62195200	12.70802500	5.44064200	H	3.20072100	13.78223000	1.79020800
H	3.63130900	12.48127600	7.20106000	H	-3.01967500	12.41071200	6.28512600
H	3.58365800	18.15253600	4.33229400	H	0.65168100	11.33056300	7.58129300
H	3.46223100	16.66686500	3.37068600	H	3.17338600	13.61872200	6.03317500
O	-3.03939300	15.34670500	3.58853600	H	-2.27714700	12.99196400	-0.54121000
H	-3.37963600	16.17243200	3.97913600	H	-2.66245500	11.75970900	0.66726900
H	-2.71851400	15.60119600	2.70348200	H	3.04372700	12.37395300	0.72172200
κ^1 N bound $\text{Me}_2\text{TpmCu}^{\text{I}}(\text{HNO}_2)$				H	3.00405500	12.15930800	2.48258500
Cu	-2.05192100	14.13216200	3.93103600	H	-2.12032000	18.62066100	3.59441400
O	-4.65830200	15.22917300	4.30244500	H	-2.01077000	18.43814800	5.34868700
O	-4.72515000	13.19374600	3.72680000	H	-2.35914000	10.81188500	6.70308100
N	-0.70439200	15.81535000	4.16937800	H	-2.29149700	12.12436800	7.88444200
N	0.60661800	15.46572200	4.03458100	H	3.18049100	12.22190300	4.93710000
N	-0.83959800	13.54442900	2.34340500	H	3.15160100	11.97259800	6.69324800
N	0.49475200	13.54253300	2.61793500	H	3.32696500	17.47712100	3.87354200
N	-0.80030500	13.10189700	5.21737000	H	3.17103600	16.01648300	2.87993500
N	0.53221900	13.27312500	4.98770900	H	-4.08043100	12.48600300	3.50115500
N	-3.97408800	14.29775900	4.01479800	κ^1 O bound $\text{Me}_2\text{TpmCu}^{\text{I}}(\text{HNO}_2)$			
C	-1.98985900	17.88635800	4.39972100	Cu	-1.35823900	-0.59469200	-0.01558200
C	-0.71573700	17.14226700	4.24109800	O	-3.31683400	-1.09552900	-0.14625600
C	0.59745100	17.65137600	4.14579900	O	-3.74526000	0.95847100	-0.03575000
C	1.42569700	16.55909800	4.00643800	N	0.35123000	-1.84840900	-0.05680100
C	2.89632900	16.47092500	3.84214000	N	1.51459400	-1.14442700	0.05734000
C	-2.30623600	12.79080900	0.53647900	N	-0.44927000	0.47763300	1.52881900
C	-0.96661300	12.97396600	1.14889500	N	0.84208300	0.81887700	1.25629000
C	0.29916700	12.60044800	0.65178200	N	-0.39679600	0.64918900	-1.40890000
C	1.21784900	12.96913600	1.61266200	N	0.92209800	0.84704800	-1.13369200
C	2.69213800	12.81685800	1.65913100	N	-4.21801400	-0.29884800	-0.14857900
C	-2.20899400	11.89383000	6.81489800	C	-0.32483500	-4.19650200	-0.14050000

C	0.70173900	-3.12951800	-0.03159600	O	-4.11977600	15.56051700	2.58777800
C	2.10205300	-3.25333000	0.10116400	O	-4.10425300	13.94145900	3.94974000
C	2.59933500	-1.96940000	0.15946900	N	-0.79061300	15.61825300	4.28316800
C	3.98720000	-1.46960800	0.30943600	N	0.52335000	15.33888500	4.04851400
C	-2.14733900	1.04857900	3.19361100	N	-0.82841000	13.48424900	2.24776800
C	-0.78714200	1.17146800	2.61070300	N	0.49825500	13.46309400	2.56263300
C	0.29472500	1.97283600	3.03500100	N	-0.75178500	12.79669700	5.12358300
C	1.32185000	1.73810000	2.14591900	N	0.56089700	13.11338200	4.93050900
C	2.68739900	2.31023700	2.06515400	N	-4.84393500	14.84894200	3.18333700
C	-1.96798300	1.23142300	-3.19197400	C	-2.16749200	17.61603200	4.60901200
C	-0.61362200	1.23470100	-2.58238700	C	-0.86627100	16.94299800	4.36472400
C	0.57924700	1.80999000	-3.06912600	C	0.40776000	17.52094400	4.17714800
C	1.54997100	1.54376900	-2.12603200	C	1.27960200	16.47380300	3.96798000
C	2.99495200	1.87397200	-2.09866200	C	2.73691500	16.46261800	3.69390900
C	1.49845300	0.30076100	0.07600800	C	-2.24690300	12.71811700	0.40751300
H	2.53955400	0.63629100	0.11417900	C	-0.92784200	12.87561500	1.06991300
H	-1.33256000	-3.76085200	-0.15206200	C	0.34365800	12.45363600	0.62591200
H	2.68087400	-4.16942700	0.14958800	C	1.23863400	12.83109600	1.60394400
H	4.28809500	-0.83439500	-0.53528000	C	2.70331400	12.62559300	1.70824500
H	-2.69337800	0.22013200	2.72380600	C	-2.07239900	11.53777800	6.75346000
H	0.32460500	2.64169800	3.88843500	C	-0.78626300	12.06763600	6.23484200
H	3.46422100	1.53547900	2.11890900	C	0.51330700	11.91907100	6.76510600
H	-2.56127700	0.38839100	-2.81505500	C	1.35657300	12.60608600	5.91822600
H	0.71824500	2.35067400	-3.99919800	C	2.82088900	12.83298800	5.97805600
H	3.61799600	0.96915300	-2.06844200	C	0.95199800	13.97477300	3.83674700
H	-2.10001600	0.86674700	4.27474000	H	2.04636900	13.98139000	3.80887500
H	-2.72596200	1.96998500	3.04224300	H	-2.91046800	16.89830700	4.97988000
H	2.84384000	3.00106000	2.90019900	H	0.66259100	18.57516500	4.19758500
H	2.83473200	2.87128300	1.13168100	H	3.28848300	15.84298200	4.41427200
H	-0.25918500	-4.89871700	0.70027200	H	-3.04897000	13.09404500	1.05580700
H	-0.19189300	-4.77943700	-1.06148500	H	0.58140000	11.93535100	-0.29695000
H	-2.51069900	2.15788500	-2.95796400	H	3.24574000	13.56824000	1.86446400
H	-1.90622700	1.15448800	-4.28405400	H	-2.90667500	11.86695900	6.12026000
H	3.25970900	2.49356600	-1.23075600	H	0.80222300	11.37554800	7.65828100
H	3.25819800	2.43317300	-3.00258500	H	3.05683900	13.89560000	6.13028400
H	4.67936100	-2.31671100	0.35596700	H	-2.28368600	13.26970700	-0.54114900
H	4.10894600	-0.88265600	1.23046200	H	-2.45077800	11.66408100	0.17903600
H	-4.54017700	1.53660300	-0.04638800	H	3.07462500	12.17349300	0.78263400
				H	2.95764300	11.94977100	2.53662100
κ^1 O(H) bound $\text{Me}_2\text{TpmCu}^{\text{I}}(\text{HNO}_2)$				H	-2.55824200	18.06872200	3.68739600
Cu	-2.03538700	13.93235500	3.92548000	H	-2.06242800	18.42090200	5.34708900

H	-2.06862100	10.44009100	6.77700300
H	-2.25754000	11.88448600	7.77828000
H	3.32890900	12.50300200	5.06159100
H	3.24333900	12.27192600	6.81806300
H	3.12872200	17.48311300	3.75711500
H	2.95406800	16.08000800	2.68677100
H	-4.75337500	13.36767000	4.41171300

Me²TpCu^I(H₂O)

Cu	-1.89205300	13.95517800	3.96036100
O	-3.98139000	13.76336300	4.06166400
N	-0.75584300	15.70189000	4.06504500
N	0.58571600	15.44697400	4.02570300
N	-0.76960800	13.23263400	2.34257800
N	0.57295800	13.38906900	2.53217400
N	-0.66890600	12.97993400	5.34206000
N	0.65835300	13.12259300	5.05875000
C	-2.25682700	17.62851100	4.30216700
C	-0.90316500	17.01693300	4.22309900
C	0.35999900	17.63324300	4.28795400
C	1.28079200	16.60438500	4.15969600
C	2.76652500	16.67427900	4.16152500
C	-2.30096700	12.41475000	0.60899700
C	-0.93662600	12.70485400	1.13020200
C	0.31337300	12.51156300	0.51758500
C	1.25030000	12.95960600	1.43919000
C	2.73296600	12.99543600	1.32464100
C	-2.09490100	11.79407300	6.94396500
C	-0.76283400	12.17107600	6.39659400
C	0.52180600	11.77969400	6.81262600
C	1.40016300	12.40390500	5.93718500
C	2.88624100	12.35042100	5.90459200
B	1.11099600	13.99580300	3.85700100
H	2.31031100	14.01613900	3.81790800
H	-3.02939300	16.84745600	4.28581500
H	0.57949700	18.68914200	4.41336900
H	3.20590900	16.07642200	4.97181600
H	-2.87584800	13.33898200	0.45295000
H	0.51382200	12.09928400	-0.46678900
H	3.12734500	14.01742500	1.40865800
H	-2.77351100	12.65813000	6.96209500

H	0.78262700	11.13146700	7.64377300
H	3.33708500	13.34370700	6.03633300
H	-2.25097200	11.88664500	-0.35058800
H	-2.87221600	11.79026000	1.31022400
H	3.03764900	12.59721700	0.34961800
H	3.22168800	12.39214300	2.10180500
H	-2.44343000	18.30907200	3.46006600
H	-2.38188000	18.21320200	5.22335800
H	-2.57337200	11.01425100	6.33346100
H	-2.00838400	11.40541700	7.96583600
H	3.26249600	11.94458200	4.95550100
H	3.25063700	11.70623000	6.71345700
H	3.08660000	17.71385200	4.29893500
H	3.19747900	16.31186000	3.21810900
H	-4.18135600	12.82958600	4.23997800
H	-4.34279500	13.92213200	3.17410100

Me²TpCu^{II}(H₂O)

Cu	-1.88893400	14.40699100	3.92511500
O	-3.37510500	13.09819300	3.76609600
N	-0.61855900	15.86319600	4.06072900
N	0.70266000	15.54613200	4.01373400
N	-0.82028200	13.64546600	2.28671800
N	0.52046600	13.53514700	2.52306000
N	-0.78984700	13.30859200	5.32089900
N	0.54766400	13.26478000	5.05051900
C	-2.06561300	17.84892400	4.23924200
C	-0.73658700	17.18930100	4.17229700
C	0.54839200	17.74767500	4.20152400
C	1.43232800	16.68085900	4.09798600
C	2.91721600	16.68615200	4.07693300
C	-2.43368000	13.08227300	0.50978700
C	-1.06043300	13.13342400	1.07791300
C	0.14373000	12.68060400	0.51748400
C	1.12458500	12.95220700	1.46115300
C	2.58673000	12.69453200	1.39546600
C	-2.37244900	12.38843500	6.96906900
C	-1.00759000	12.56486300	6.40737000
C	0.20874600	12.02526900	6.85164700
C	1.17295300	12.49128500	5.96852200
C	2.63793600	12.24263700	5.96381700

B 1.12324700 14.06083400 3.85164400
 H 2.31601100 13.96846100 3.82946000
 H -2.87502500 17.10806700 4.21130500
 H 0.80536500 18.79812600 4.28750500
 H 3.33701800 16.09231300 4.89977400
 H -3.03829900 13.93245500 0.85130900
 H 0.28593200 12.22031900 -0.45504200
 H 3.16818000 13.62300000 1.47446200
 H -2.99231400 13.27645700 6.78971300
 H 0.37031900 11.38351700 7.71176200
 H 3.21068600 13.17481900 6.06012500
 H -2.40149500 13.10476600 -0.58606400
 H -2.95394800 12.15928400 0.80199000
 H 2.83466300 12.22034300 0.43907800
 H 2.92189200 12.02683300 2.20021600
 H -2.20636900 18.53876100 3.39712500
 H -2.17093700 18.43506300 5.16105400
 H -2.88213500 11.52418900 6.52050800
 H -2.32919400 12.21483100 8.05085200
 H 2.96663000 11.74789700 5.04030200
 H 2.90321900 11.59405900 6.80640400
 H 3.28446600 17.71353100 4.17729200
 H 3.31174800 16.27437500 3.13827500
 H -3.98461900 13.33813800 3.04568200
 H -3.92135000 13.08996100 4.57216700

κ^1 N bound $\text{Me}_2\text{TpCu}^{\text{I}}(\text{HNO}_2)$

Cu -1.92746000 14.06225500 3.94647200
 O -4.47928700 14.61638100 5.04663400
 O -4.64728700 13.81449600 3.09240500
 N -0.73234900 15.72390700 4.03108500
 N 0.60550700 15.46158700 3.98316500
 N -0.78290100 13.29973100 2.29906500
 N 0.56306800 13.39699300 2.51001200
 N -0.73848300 13.02625800 5.25571900
 N 0.60059500 13.15861300 5.03174800
 N -3.85403000 14.11663600 3.93155700
 C -2.22703700 17.65787200 4.27872600
 C -0.87748000 17.04284200 4.16507600
 C 0.38714400 17.65276800 4.20051000
 C 1.30446100 16.61711300 4.08273300

C 2.78976000 16.67760400 4.05591600
 C -2.31479900 12.48477000 0.56005700
 C -0.95335300 12.73728000 1.10272700
 C 0.29835900 12.46276400 0.52250500
 C 1.23770300 12.89523700 1.44606600
 C 2.72203600 12.85318600 1.36466600
 C -2.24255200 11.96035700 6.87881300
 C -0.88956800 12.26833800 6.34272700
 C 0.37244200 11.89440700 6.83331000
 C 1.29445100 12.47934500 5.97568200
 C 2.77967400 12.41735500 6.00953600
 B 1.10618900 13.99990400 3.82898200
 H 2.30511600 13.99100300 3.81233800
 H -2.96463100 17.10340800 3.68294500
 H 0.60952700 18.71094000 4.29642800
 H 3.23871800 16.09752700 4.87368500
 H -3.08052200 12.82897600 1.26784300
 H 0.49720900 12.00853500 -0.44336800
 H 3.16579100 13.85625100 1.42604000
 H -2.57332800 12.72507800 7.59642600
 H 0.59012100 11.27715800 7.69937300
 H 3.22963200 13.41429400 6.11227300
 H -2.47081300 13.00830300 -0.39290900
 H -2.48093000 11.41549300 0.37110500
 H 3.02740700 12.40719900 0.41092200
 H 3.16054600 12.25250200 2.17335100
 H -2.21598900 18.69780500 3.93046800
 H -2.57926000 17.66456800 5.32035600
 H -2.98529600 11.92041300 6.07066000
 H -2.25158800 10.99693300 7.40280400
 H 3.19198400 11.96425900 5.09752000
 H 3.10477700 11.81166600 6.86338000
 H 3.11917700 17.71793300 4.15972700
 H 3.19923200 16.28664700 3.11439000
 H -3.75498900 14.83452100 5.67520700

κ^1 O bound $\text{Me}_2\text{TpCu}^{\text{I}}(\text{HNO}_2)$

Cu -1.85934400 13.97063000 3.90790800
 O -3.86119400 13.88702100 3.65937600
 O -4.02883500 14.72466400 5.57937600
 N -0.71710300 15.68217000 4.00306700

N	0.62411800	15.43063700	3.97591000	H	3.19091400	11.77836500	6.81931000
N	-0.71824300	13.22327900	2.29035600	H	3.11613100	17.71051400	4.19138800
N	0.62300900	13.35960300	2.50179800	H	3.22819800	16.28444000	3.14257300
N	-0.68425300	12.96859500	5.26523800	H	-4.74490100	15.00420600	6.19079300
N	0.65188500	13.12286000	5.03069600				
N	-4.66228700	14.26011300	4.47721500				
C	-2.23071200	17.60336800	4.20241300	κ^1 O(H) bound $^{Me_2}TpCu^I(HNO_2)$			
C	-0.87315400	16.99998900	4.12600100	Cu	-1.87640200	14.00109800	3.96748900
C	0.38670800	17.62168100	4.17846600	O	-4.10654600	15.07139200	2.36276300
C	1.31319100	16.59320500	4.08049700	O	-3.95257000	13.97673900	4.16380800
C	2.79837400	16.66740200	4.07832800	N	-0.72442100	15.72739900	4.06554700
C	-2.23724600	12.38665200	0.56019000	N	0.61206300	15.45087900	4.02950600
C	-0.87430600	12.66721700	1.09020600	N	-0.79661000	13.26379800	2.35669000
C	0.38278500	12.43545900	0.50571200	N	0.55001600	13.38904700	2.54753400
C	1.31157000	12.88894100	1.43313500	N	-0.70058200	13.00737600	5.35041300
C	2.79649600	12.89320600	1.34794400	N	0.63081200	13.13077500	5.07727100
C	-2.15642700	11.84110100	6.87363800	N	-4.76796900	14.58077300	3.20783500
C	-0.81258200	12.18888000	6.33855600	C	-2.20092400	17.67635400	4.23889600
C	0.45970800	11.82475500	6.81284900	C	-0.85321100	17.04717500	4.19414400
C	1.36472400	12.43676500	5.95712100	C	0.41830600	17.64501400	4.24698100
C	2.85114800	12.39495700	5.97897100	C	1.32447300	16.59933400	4.13954900
B	1.14412800	13.97462100	3.82851900	C	2.81095800	16.64460500	4.14427500
H	2.34360800	13.98464400	3.81697600	C	-2.34817900	12.49999700	0.61602800
H	-2.97493200	16.93960400	3.74155000	C	-0.97836800	12.74540800	1.14273500
H	0.60026800	18.68204700	4.27144500	C	0.26784800	12.52450200	0.52954600
H	3.23968200	16.08883200	4.90136900	C	1.21487500	12.94655800	1.45155400
H	-2.80837000	11.74685900	1.24769900	C	2.69787800	12.94380700	1.33889800
H	0.59344100	11.99513100	-0.46425300	C	-2.15981400	11.88388900	6.96400000
H	3.20937100	13.90903800	1.41512900	C	-0.81598900	12.21693000	6.41623400
H	-2.46002500	12.52612400	7.67823500	C	0.45921100	11.81549100	6.84930900
H	0.69470000	11.19589100	7.66609700	C	1.35434700	12.41597000	5.97332900
H	3.28829900	13.39596900	6.09700200	C	2.83967600	12.34216000	5.95373300
H	-2.81328100	13.31337900	0.42690400	B	1.10549900	13.98637200	3.87007000
H	-2.18570500	11.87959700	-0.41051800	H	2.30461100	13.97858600	3.83092500
H	3.11286500	12.46444500	0.38981300	H	-2.93763900	16.98613300	4.67281000
H	3.25659100	12.30029700	2.15030200	H	0.65273300	18.69980600	4.35317300
H	-2.26542600	18.57084700	3.68593500	H	3.23771500	16.04900600	4.96292500
H	-2.53779700	17.77789000	5.24354900	H	-3.07054700	12.41840300	1.43972800
H	-2.91631000	11.89957900	6.08218300	H	0.45938300	12.10893800	-0.45509900
H	-2.16783800	10.82524700	7.28807700	H	3.11829000	13.95532600	1.42257700
H	3.26391400	11.96485200	5.05603400	H	-2.72719400	12.79399600	7.20512300
				H	0.70360300	11.17436800	7.69082300

H	3.30232000	13.33049800	6.08182000	C	5.54936700	6.86357200	2.06094600
H	-2.68059800	13.31743800	-0.03989500	C	4.20955700	7.02752300	-0.06442400
H	-2.38984900	11.57420300	0.02817500	C	5.67320400	8.33481900	2.29690200
H	2.99387300	12.53632700	0.36510700	C	5.44889300	8.68259700	3.76349500
H	3.16863400	12.32937400	2.11851300	C	7.03686800	8.82893500	1.81347500
H	-2.55252500	17.94651800	3.23265300	H	4.16699900	1.68636900	4.33540400
H	-2.19286500	18.59467700	4.83905600	H	3.18406500	1.42747500	6.53809200
H	-2.75574700	11.30973600	6.24001100	H	4.36113700	1.65543100	7.85313800
H	-2.07547000	11.28584900	7.87904500	H	3.12923300	2.90907600	7.52094700
H	3.21806500	11.92434600	5.01067300	H	5.31991100	3.79924300	8.44229200
H	3.18853700	11.69958600	6.77063700	H	7.77831900	3.79167600	7.99340900
H	3.14831400	17.68014000	4.27000500	H	7.65200800	5.39825000	7.24848500
H	3.23784800	16.26374300	3.20632100	H	7.29919800	5.19174900	8.97864700
H	-4.55155900	13.58758800	4.83736100	H	5.01173400	6.25867200	8.68550900
ⁱ PrTICCu ⁺ (H ₂ O)				H	5.29586500	6.47735500	6.94310400
Cu	7.41944300	5.69081900	4.48224400	H	3.85769600	5.59722700	7.50469100
O	5.62955200	2.38608400	2.03170900	H	8.26892600	1.47262400	1.59815100
N	6.20680900	4.13121500	5.23626000	H	11.63294600	1.77639900	2.81537600
N	4.68630600	2.79448500	6.10828100	H	10.66486800	1.08910000	1.49115000
N	8.52374400	4.26688800	3.35230100	H	11.55378400	2.61023100	1.23445000
N	9.80745400	2.74345300	2.40835500	H	11.85388100	4.24273700	3.03125700
N	6.07584600	5.91394300	2.82104100	H	11.80169400	6.62522300	3.68526700
N	4.91159300	6.31799100	0.99244500	H	10.71277400	6.35284500	2.30498900
C	6.21247200	3.40797100	2.81950700	H	10.04540300	6.54390600	3.94133700
C	5.72546700	3.30277100	4.24768400	H	11.34829300	3.23635100	5.26340900
C	4.77830900	2.46820400	4.77038400	H	12.14025600	4.81913200	5.43910700
C	5.56542900	3.80229400	6.34807600	H	10.38560700	4.66943300	5.69280700
C	3.79314100	2.16511400	7.06724700	H	4.60037000	4.28641700	0.34504300
C	5.72876100	4.47332900	7.67409900	H	3.34123800	7.56221800	0.33615200
C	7.19838300	4.72462500	7.98986800	H	4.87846200	7.73848900	-0.56140600
C	4.92396300	5.77374800	7.70370900	H	3.86393100	6.29601500	-0.79959800
C	7.72207600	3.31585800	2.76198400	H	4.89522200	8.83602000	1.70119500
C	8.50246400	2.36367000	2.16918700	H	6.21452100	8.21354200	4.39851800
C	9.77559900	3.89987300	3.12084600	H	5.50647200	9.76965900	3.90869200
C	10.98806300	2.02035600	1.96406400	H	4.46559900	8.34266400	4.11643200
C	10.99363400	4.61935700	3.60480500	H	7.84729300	8.34645700	2.38133200
C	10.88031000	6.12033800	3.36545800	H	7.19585900	8.60819000	0.74861800
C	11.23139000	4.31443000	5.08412300	H	7.12486100	9.91507700	1.95252700
C	5.75851400	4.71672000	2.22107900	H	5.87353100	1.52269300	2.40678800
C	5.03706000	4.94643000	1.08472000	O	8.27209700	7.24466300	5.62459000
				H	7.61390900	7.62111200	6.23225100

H 8.51382000 7.98441200 5.04260000

^{iPr}TICCu^{II}(H₂O)

Cu 7.43528300 5.73044100 4.30974500

O 5.64368900 2.28808000 2.08426400

N 6.05713200 4.28441200 5.16397100

N 4.71022600 2.85863700 6.15891400

N 8.51328900 4.28581800 3.25349100

N 9.83569400 2.77947000 2.36322600

N 6.22216000 5.81151200 2.78699100

N 4.94393500 6.28593600 1.08283600

C 6.22841700 3.31890700 2.84434600

C 5.73725500 3.28074900 4.27412400

C 4.90221100 2.38800900 4.87720400

C 5.41058900 4.01124600 6.29235500

C 3.86093900 2.23279000 7.16167100

C 5.42720100 4.82634100 7.54427800

C 6.64908200 4.48075300 8.39509700

C 5.33041100 6.31395800 7.22894700

C 7.73769100 3.25298500 2.77204600

C 8.54775300 2.30853100 2.21651100

C 9.77838900 3.98572900 2.97652500

C 11.03074100 2.10969800 1.87093400

C 10.97604200 4.84122000 3.24027200

C 10.65736300 6.31119500 2.99441000

C 11.54000000 4.59458900 4.63942100

C 5.78771800 4.62536400 2.23665200

C 4.98842100 4.90774100 1.17330500

C 5.70351300 6.80717200 2.07180200

C 4.20182200 7.03418200 0.07783300

C 5.85115300 8.26848000 2.33912100

C 4.74420300 8.73250800 3.28782200

C 7.22583700 8.62530700 2.88965900

H 4.41914400 1.48357900 4.52693600

H 3.50569400 1.27989000 6.76139600

H 4.42680300 2.04133100 8.07905000

H 2.99780800 2.86848800 7.38701700

H 4.53242900 4.54922000 8.12178300

H 6.65615300 3.41627600 8.66712600

H 7.58691300 4.68981300 7.86298500

H 6.64464400 5.06670800 9.32379600

H 5.40001400 6.90353700 8.15216800

H 6.13452000 6.64332700 6.55450800

H 4.37701400 6.55543500 6.74062700

H 8.34132900 1.36408200 1.72714600

H 11.80914100 2.10827100 2.63987900

H 10.77058800 1.07540000 1.63173700

H 11.40512000 2.60362000 0.96750700

H 11.74589200 4.54189700 2.51257900

H 11.53808900 6.92966800 3.21021800

H 10.36440700 6.48660400 1.95050600

H 9.83276100 6.66435600 3.63045700

H 11.81859000 3.54158800 4.78202300

H 12.43842100 5.20613500 4.79619100

H 10.80796300 4.85424400 5.41539300

H 4.45727500 4.27410700 0.47415300

H 3.43298900 7.65484400 0.54955100

H 4.88021100 7.66571000 -0.50502100

H 3.72074100 6.31791900 -0.59266200

H 5.72223400 8.78519800 1.37604200

H 4.84099100 8.23294600 4.26334300

H 4.81570600 9.81570600 3.45239200

H 3.74399100 8.51331300 2.89144500

H 7.36666100 8.23593400 3.91245700

H 8.03749000 8.24601500 2.25498300

H 7.32584400 9.71629600 2.95377700

H 5.90161000 1.42758500 2.45805400

O 8.65239500 5.98993800 5.85795700

H 8.18154700 6.36976900 6.62107900

H 9.35417400 6.63503000 5.65826700

κ^1 N bound ^{iPr}TICCu^I(HNO₂)

Cu 7.28425100 5.79861600 4.54322100

O 5.58482900 2.43462900 2.05766200

N 6.13470000 4.18386700 5.26565400

N 4.74542800 2.72344100 6.15638700

N 8.48221800 4.27367200 3.42505300

N 9.75936900 2.80294300 2.38745900

N 6.09891200 5.96055000 2.82392700

N 4.91805800 6.35225300 1.00448100

C 6.17283100 3.44591300 2.85274900

C 5.69583700 3.32691700 4.28014000

C	4.82940600	2.41818000	4.81479900	H	10.18245300	4.83357500	5.68203700
C	5.54895300	3.79055500	6.39224900	H	4.53076700	4.31628400	0.41706100
C	3.92806800	2.01039300	7.12549700	H	3.35986300	7.61031200	0.34792900
C	5.69075600	4.43191200	7.73546900	H	4.88599000	7.74435600	-0.57552900
C	7.15391600	4.66952900	8.09079400	H	3.84481400	6.31456100	-0.77173200
C	4.85430700	5.71038200	7.78927900	H	4.91941800	8.86830700	1.68224500
C	7.68010100	3.35263100	2.79183900	H	6.76038000	8.51527000	4.09048700
C	8.45352300	2.43373300	2.14128700	H	5.80630300	9.94343800	3.66640400
C	9.73281000	3.91958900	3.15970700	H	4.98115900	8.46261300	4.20771400
C	10.93515500	2.10285700	1.89526800	H	7.93369400	8.33747600	1.89632200
C	10.95302000	4.62910700	3.65138300	H	7.03003000	8.51879200	0.37483500
C	10.93054000	6.09270300	3.21751700	H	7.18380200	9.89798000	1.48641100
C	11.07840900	4.46252600	5.16552800	H	5.85123900	1.56566600	2.40329400
C	5.73214400	4.75754500	2.25828200	O	7.47314800	7.91545800	6.53547900
C	4.99898100	4.98205400	1.13140800	H	6.53154500	7.77012400	6.29817000
C	5.59251100	6.90932800	2.04194500	N	8.19859900	7.10122500	5.70893400
C	4.21298100	7.05418000	-0.05608900	O	9.36679500	7.22055000	5.91435500
C	5.77977700	8.38658200	2.17171700				
C	5.82649700	8.84680700	3.61970100				
C	7.05252100	8.80860900	1.43416500				
H	4.27242000	1.59414600	4.38520700	κ^1 O bound ^{ipr} TiCCu ^l (HNO ₂)			
H	3.36001200	1.24206800	6.59471200	Cu	7.39174600	5.67460100	4.43961400
H	4.55594000	1.52727700	7.88178400	O	5.58963400	2.34694100	2.02863000
H	3.22513800	2.69395400	7.61372100	N	6.09888000	4.23186000	5.16692900
H	5.27880400	3.73244200	8.47797000	N	4.67887600	2.83241900	6.10042200
H	7.71398200	3.72535700	8.12643300	N	8.47291500	4.24873100	3.34413300
H	7.64980900	5.32000000	7.35963900	N	9.75943000	2.76545400	2.34482100
H	7.23190500	5.14920000	9.07544200	N	6.04353500	5.89966400	2.69482100
H	4.99952500	6.23150400	8.74508400	N	4.85306500	6.24559100	0.87049100
H	5.12774500	6.39772500	6.97653700	C	6.16338000	3.39663400	2.78405000
H	3.78338400	5.48930700	7.67954600	C	5.67762600	3.32958800	4.21493800
H	8.21369300	1.57336700	1.52759300	C	4.79314600	2.45499600	4.77818100
H	11.56818900	1.78068400	2.72938400	C	5.47760100	3.91249400	6.29424500
H	10.60401400	1.21855700	1.34429700	C	3.84464100	2.17123000	7.09112500
H	11.51494400	2.74293400	1.22146600	C	5.65752000	4.59739200	7.61115500
H	11.82924700	4.15361500	3.18654800	C	6.96868700	4.14729400	8.25669600
H	11.79969100	6.62702200	3.62493100	C	5.59993700	6.11274600	7.45773300
H	10.95849200	6.18019900	2.12269200	C	7.67314400	3.30992200	2.73025500
H	10.02379900	6.60105900	3.57078900	C	8.45614300	2.38347800	2.10311400
H	11.20888400	3.40496600	5.43552200	C	9.72746500	3.89907700	3.09054200
H	11.94585600	5.02027900	5.54433700	C	10.94162100	2.06518000	1.86835300
				C	10.94949000	4.60724600	3.58073600
				C	10.82297500	6.11426900	3.39126100

C 11.22124300 4.23459300 5.03909200
 C 5.70749900 4.68513600 2.14463700
 C 4.97007400 4.87721800 1.01118300
 C 5.51122800 6.82448100 1.90888800
 C 4.14751100 6.92020800 -0.20703900
 C 5.62038300 8.30118000 2.12162600
 C 5.11669000 8.68748400 3.51002400
 C 7.05702200 8.76876600 1.89207900
 H 4.23165300 1.61868300 4.37897400
 H 3.33705500 1.33242600 6.60793800
 H 4.45411400 1.78804000 7.91697700
 H 3.08983700 2.86120900 7.48327400
 H 4.82879800 4.28585900 8.26467500
 H 6.98834900 3.05952200 8.41255000
 H 7.82750100 4.41346000 7.62273600
 H 7.10310400 4.63233000 9.23314100
 H 5.71330300 6.59834700 8.43628800
 H 6.40645100 6.47213500 6.80301300
 H 4.64589800 6.44002500 7.02190900
 H 8.22366500 1.50935400 1.50639100
 H 11.59817500 1.80568200 2.70574000
 H 10.62090500 1.14383300 1.37503800
 H 11.49239100 2.67959800 1.14778500
 H 11.80018500 4.25870700 2.97609000
 H 11.72061100 6.62197700 3.76897800
 H 10.70099400 6.37724100 2.33159400
 H 9.95350500 6.50835700 3.93330800
 H 11.39913700 3.15574700 5.15131500
 H 12.10844000 4.76480900 5.41170200
 H 10.36863100 4.50216100 5.67964900
 H 4.52236100 4.19344500 0.30025000
 H 3.29339300 7.48580900 0.18110800
 H 4.82094700 7.59720900 -0.74399400
 H 3.78042200 6.16362000 -0.90552600
 H 4.97859300 8.79569400 1.37741800
 H 5.71989500 8.21466800 4.29761900
 H 5.17656000 9.77568800 3.64739900
 H 4.07120500 8.38424200 3.65756000
 H 7.74718900 8.28490300 2.59866100
 H 7.39731300 8.53599300 0.87322000
 H 7.13370800 9.85522000 2.03582600

H 5.85046900 1.49690500 2.42312700
 O 9.21007600 6.71254900 6.57449300
 H 9.82483500 7.04128800 7.26618400
 N 8.72915200 7.82027200 5.96765900
 O 7.96647200 7.52227900 5.08736100

κ^1 O(H) bound iPr TICCu^I(HNO₂)

Cu 7.37345200 5.75655900 4.41271700
 O 5.63419800 2.38480200 2.05443900
 N 6.16199400 4.21558400 5.21856100
 N 4.73133900 2.81305200 6.13551700
 N 8.51128300 4.28880000 3.39231700
 N 9.79772400 2.82201700 2.36561100
 N 6.06689400 5.93684500 2.73921200
 N 4.82805600 6.27833600 0.94779500
 C 6.19978100 3.43201200 2.82041500
 C 5.71844300 3.34213500 4.25203500
 C 4.82477600 2.46702400 4.80261300
 C 5.55516300 3.87163000 6.34502600
 C 3.88219600 2.15543100 7.11591400
 C 5.73276900 4.56944500 7.65521100
 C 7.20963200 4.62321700 8.03787300
 C 5.10711100 5.96217600 7.59143200
 C 7.71136200 3.36099000 2.75934600
 C 8.49480400 2.44819000 2.11228400
 C 9.76439100 3.93898300 3.13833200
 C 10.98062900 2.15443500 1.84825000
 C 10.99206600 4.60013800 3.67745700
 C 10.77935800 6.09264100 3.87731100
 C 11.40143200 3.93770500 4.99526500
 C 5.72401600 4.71962900 2.19537800
 C 4.95585500 4.91053100 1.08312900
 C 5.50866700 6.86056800 1.96803600
 C 4.08963600 6.95362100 -0.10706800
 C 5.65824700 8.33860700 2.13844200
 C 5.50154700 8.73833800 3.60099700
 C 7.00294800 8.78455400 1.55980700
 H 4.25162700 1.64466600 4.39104300
 H 3.32767300 1.35971000 6.61172400
 H 4.48435000 1.71351800 7.91694600
 H 3.16687800 2.86642300 7.54403600

H	5.19973600	3.99081200	8.42422300
H	7.62160700	3.61596100	8.18752200
H	7.80642100	5.10913700	7.25176100
H	7.34329600	5.18778200	8.97047900
H	5.24218300	6.48980900	8.54542300
H	5.56954800	6.56521100	6.79553300
H	4.02937900	5.90717500	7.38254800
H	8.26245500	1.58800700	1.49543600
H	11.66281900	1.89021400	2.66301600
H	10.66680100	1.23746900	1.34228600
H	11.50309000	2.79478300	1.12865800
H	11.80148600	4.45114400	2.94523400
H	11.71081400	6.56683400	4.21422900
H	10.45269600	6.59101600	2.95402200
H	10.01314300	6.26702400	4.64587800
H	11.57905600	2.85969400	4.88051400
H	12.32251200	4.39348200	5.38346000
H	10.61136600	4.07203600	5.75034400
H	4.48948600	4.22535100	0.38579000
H	3.23192400	7.49676600	0.30465300
H	4.73982500	7.65172000	-0.64542100
H	3.72528400	6.19980000	-0.80990400
H	4.85901100	8.82797200	1.56139800
H	6.21364100	8.19536200	4.23663400
H	5.68229200	9.81462200	3.72564300
H	4.49110800	8.51601900	3.97055800
H	7.83286500	8.24687500	2.03976100
H	7.05775700	8.58796600	0.47984400
H	7.15543700	9.86111900	1.71801200
H	5.89796200	1.53386200	2.44494500
O	7.96571100	7.34423200	5.78209200
H	7.76628700	7.36490100	6.74359800
N	8.60013800	8.55618900	5.51574700
O	8.86373400	8.64464900	4.37068700