

# The Electronic Structure of the Metal Active Site Determines the Geometric Structure and Function of the Metalloregulator NikR

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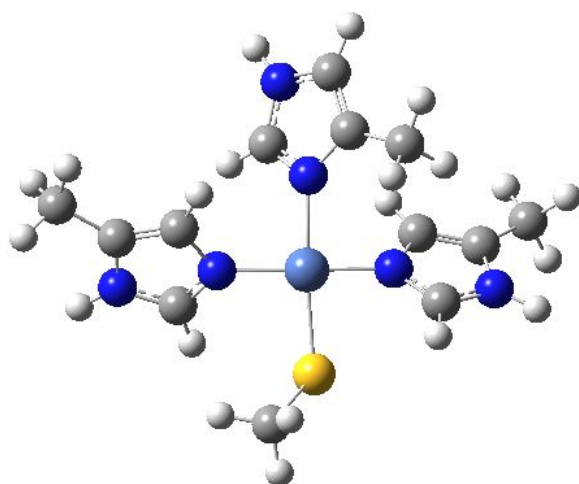


Figure S1 Ni site from the NikR proteins (PDB code 2HZV), 3 His and 1Cys ligands with the  $\alpha$  carbons.

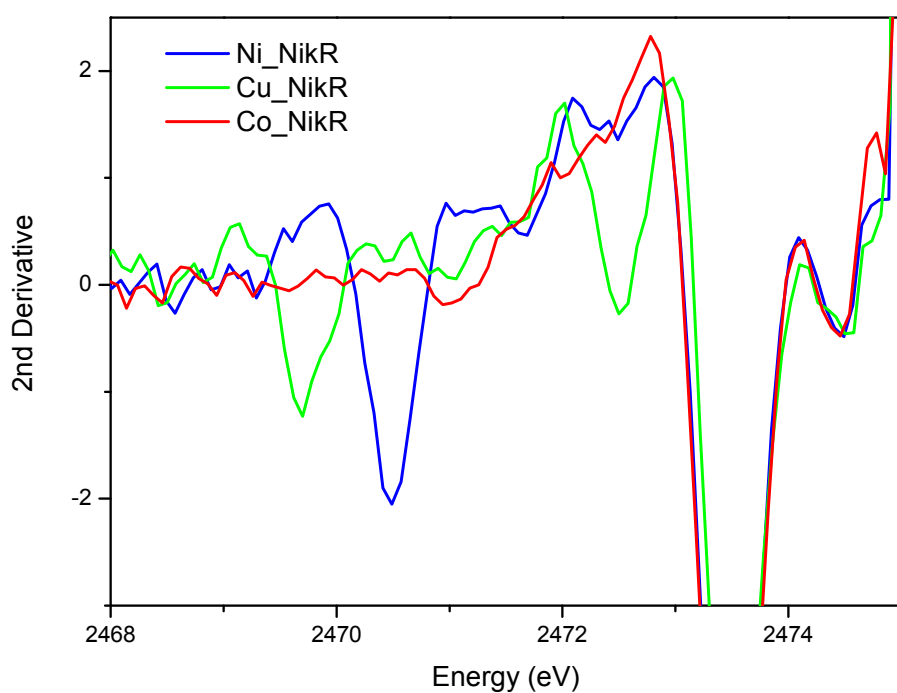


Figure S2 2<sup>nd</sup> derivatives of the S K-edge XAS of the NikR Co, Ni and Cu proteins variants from 2468 eV to 2475 eV.

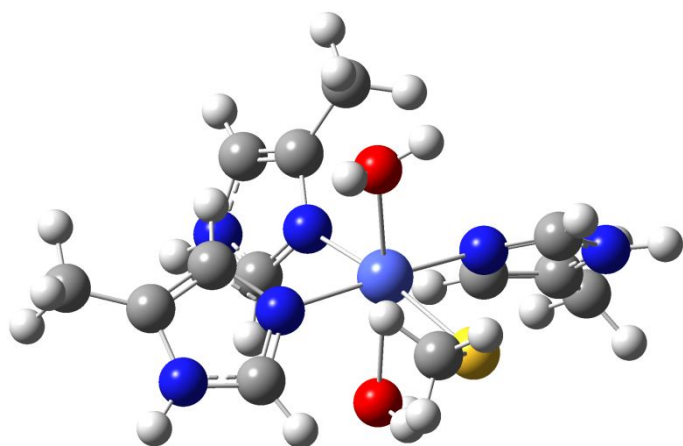


Figure S3 Geometry optimized structure of the high spin 6 coordinate Co(II)-NikR site.

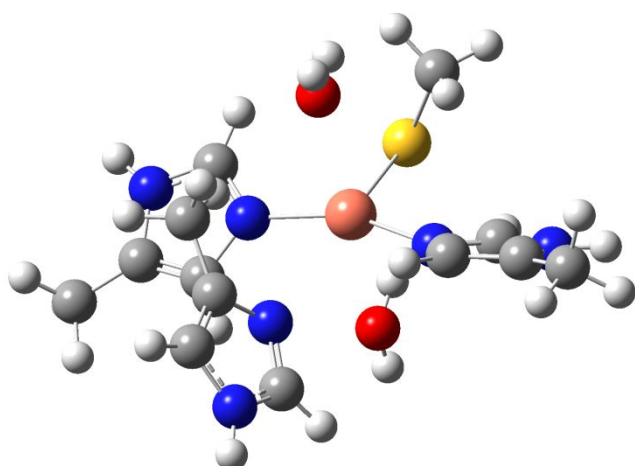


Figure S4 Geometry optimized structure of the Cu(I)-NikR site. It optimized to a 3 coordinate site, from an initial 6 coordinate structure.

Cartesian coordinates for the DFT calculation of Ni-NikR, singlet, optimized structure

C	-1.97468300	2.01685400	0.92772800
C	-2.36742700	3.42458000	1.32795000
C	-1.80024900	4.38049100	2.13798300
N	-3.52857100	4.02931300	0.86655000
C	-3.62053600	5.27654600	1.38444800
N	-2.58617200	5.53486300	2.16610100
C	0.59682600	6.04567500	4.91332800

C	-0.74692500	5.62615400	5.41265100
C	-1.04552800	4.80593800	6.46810800
N	-1.93978400	6.04303800	4.83457500
C	-2.92682100	5.49675900	5.52927000
N	-2.42308600	4.74009200	6.52749200
C	-2.86674600	8.41942500	0.17430500
S	-3.46290400	8.57610100	1.89809200
C	-1.96037000	10.24459600	7.72348500
C	-1.91423100	9.85687900	6.29371100
C	-2.77847100	9.13481800	5.50930600
N	-0.76736900	10.00415000	5.54056100
C	-0.92712100	9.34115300	4.37981200
N	-2.11486500	8.76201600	4.35623900
H	-2.74898800	1.29573300	1.20436200
H	-1.80610100	1.94151000	-0.14989100
H	-0.88428000	4.30906500	2.70033000
H	-4.20324100	3.61307900	0.24188800
H	-4.43058400	5.95798600	1.18103700
H	1.38704000	5.51981100	5.45026500
H	0.75983100	7.11772700	5.04734700
H	-0.41324300	4.27796900	7.16320200
H	-3.97790200	5.65199500	5.33410200
H	-2.96594600	4.21504500	7.19576100
H	-3.50857100	9.05249600	-0.43446600
H	-2.91551700	7.40241600	-0.21825300
H	-2.95553200	10.06878600	8.13279400
H	-1.72157300	11.29870500	7.88544200
H	-3.76925600	8.76583700	5.73339600
H	0.06795700	10.54648300	5.73549800
H	-0.17938200	9.31253100	3.60408000
H	-1.25127700	9.65109400	8.30869000
H	0.72095000	5.83270700	3.84789200
H	-1.05289200	1.73038300	1.43185800
H	-1.84792900	8.77862600	0.08099400
O	-5.45653200	7.06850200	4.26813700
H	-5.21833800	7.49080000	3.42219300
H	-6.38953500	7.24875100	4.43295500
O	1.69003900	11.17463600	4.73027500
H	2.57480000	10.86855900	4.96981600
H	1.78653500	12.06010300	4.34553000
Ni	-2.39657300	7.21705300	3.29029200

Cartesian coordinates for the DFT calculation of Ni-NiR, triplet, optimized structure

C	-1.97456700	2.01694700	0.92701100
C	-2.42195200	3.37088000	1.32853000
C	-1.97135500	4.23911500	2.28402000
N	-3.47272800	4.03200700	0.71965700
C	-3.61483100	5.24673100	1.29879600
N	-2.71454500	5.40513100	2.25487600
C	1.10270100	6.02187200	4.31340100
C	-0.04760800	5.74880400	5.22691500
C	-0.00677200	5.13696600	6.45208100
N	-1.36408700	6.09433400	4.93973200
C	-2.08490100	5.70021500	5.97553300
N	-1.30581700	5.11454900	6.91233400
C	-2.86656100	8.41891200	0.17195300
S	-3.79441400	8.47923500	1.73953700
C	-1.96057400	10.24494800	7.72300700
C	-1.97776800	9.93746900	6.28158200
C	-2.77754400	9.13391700	5.51008100
N	-0.90367400	10.27110000	5.47897700
C	-1.04264100	9.63130100	4.29728400
N	-2.14444800	8.91402600	4.30993100
H	-2.76757700	1.27123000	1.04094600
H	-1.64331200	1.98820100	-0.11579100
H	-1.17788900	4.09082100	2.99848700
H	-4.03649500	3.67682300	-0.03872300
H	-4.33865100	5.99560700	1.01169700
H	2.04416000	5.75137800	4.79381800
H	1.15761100	7.07732200	4.03951600
H	0.81233800	4.72911600	7.02169500
H	-3.14809200	5.83677700	6.08762900
H	-1.62118700	4.73566400	7.79231900
H	-3.50564800	8.76454800	-0.64314400
H	-2.53043100	7.41011900	-0.09554400
H	-2.90347400	9.95962300	8.19213500
H	-1.81050400	11.30936000	7.93089300
H	-3.69293500	8.63467000	5.77868500
H	-0.15494600	10.89912000	5.72984200
H	-0.33242000	9.68385200	3.48987900
H	-1.16114300	9.69541800	8.23095900
H	1.03993600	5.43453200	3.39004300
H	-1.13520200	1.69723400	1.54563000
H	-2.00757500	9.10325700	0.17491200
O	-4.39731700	6.78314100	4.28716500
H	-4.96160600	7.39471700	3.78875100
H	-4.63148900	5.90356600	3.96463000

O	-0.57970200	7.60164100	2.11304200
H	-0.90916300	7.99199600	1.29159400
H	-0.05192300	6.83313100	1.86809800
Ni	-2.39759600	7.21802300	3.29306500

Cartesian coordinates for the DFT calculation of Co-NikR, doublet, optimized

structure

C	-1.97462400	2.01705800	0.92717500
C	-2.40464800	3.40257900	1.33135100
C	-1.89248900	4.33586900	2.19886100
N	-3.53577800	4.01478200	0.81273800
C	-3.66289400	5.24876200	1.35669000
N	-2.67848300	5.48661900	2.20534500
C	0.60067800	6.10064400	5.13759900
C	-0.76800100	5.68882500	5.56959500
C	-1.11765300	4.91220800	6.64203300
N	-1.92661300	6.04149900	4.88760900
C	-2.94148700	5.48935200	5.53624300
N	-2.49219000	4.79843400	6.60536500
C	-2.86665600	8.41898800	0.17272400
S	-3.56776200	8.56663300	1.85555800
C	-1.96050400	10.24484000	7.72332200
C	-1.95049900	9.90426200	6.28505600
C	-2.77788200	9.13448300	5.50969200
N	-0.82248600	10.12308500	5.51643000
C	-0.95326200	9.44416100	4.35640800
N	-2.10378000	8.80034900	4.35126600
H	-2.73910700	1.27333900	1.16900400
H	-1.77188300	1.95700000	-0.14578600
H	-1.02445900	4.24281100	2.83141900
H	-4.17093600	3.61037700	0.14074000
H	-4.45505200	5.93975300	1.11726700
H	1.34011200	5.81824500	5.88850300
H	0.66730300	7.17927000	4.98445900
H	-0.52202400	4.44062800	7.40637200
H	-3.98007100	5.59456100	5.25769400
H	-3.06626600	4.28920000	7.25962600
H	-3.58333900	8.83028100	-0.54013200
H	-2.65987300	7.38601700	-0.12041600
H	-2.94477500	10.06388700	8.15758000
H	-1.71274400	11.29365000	7.91534600

H	-3.74080300	8.71115000	5.74381100
H	-0.04155200	10.70802900	5.77250000
H	-0.21065200	9.41036600	3.57806000
H	-1.24060200	9.62893100	8.27171200
H	0.89353800	5.61676200	4.19997200
H	-1.06174800	1.73891700	1.45441800
H	-1.95473500	9.01675800	0.07235400
O	-5.36646700	7.02254000	4.05544800
H	-5.21492600	7.45311200	3.19360400
H	-6.24178100	7.29259100	4.35638200
O	-0.35327800	7.50810500	2.14496100
H	-0.66827800	7.84720500	1.29755600
H	0.22181100	6.75982900	1.94799600
Co	-2.39717700	7.21737800	3.29220300

Cartesian coordinates for the DFT calculation of Co-NikR, quartet, optimized

structure

C	-1.97455700	2.01697200	0.92696300
C	-2.40213900	3.41082800	1.33948200
C	-1.75464700	4.47946400	1.91582100
N	-3.70835600	3.85728500	1.19168100
C	-3.80750000	5.12375300	1.66540500
N	-2.63684300	5.54087100	2.11768800
C	-0.31893200	5.50258700	5.67186100
C	-1.80252700	5.37706200	5.77154100
C	-2.54824000	4.68907300	6.69079200
N	-2.67046200	5.98687300	4.87558200
C	-3.90252200	5.67515500	5.24757200
N	-3.87001300	4.88911500	6.34551700
C	-2.86654100	8.41876600	0.17186400
S	-2.87437800	8.90523000	1.90973500
C	-1.96057900	10.24493300	7.72305000
C	-1.91163900	9.82326500	6.32052800
C	-2.77747500	9.13386700	5.51005800
N	-0.69766200	9.84417600	5.66404000
C	-0.81367600	9.13704300	4.52670400
N	-2.04128500	8.66340300	4.44348400
H	-2.52748000	1.25344500	1.48079500
H	-2.13597600	1.84889900	-0.14119000
H	-0.71663900	4.56059500	2.19438600
H	-4.46754800	3.33289900	0.78323400
H	-4.72693600	5.68922000	1.70807800
H	0.17053000	4.92576700	6.45793800

H	0.00152400	6.54322000	5.76898200
H	-2.26093700	4.08485800	7.53556800
H	-4.80173000	6.00963000	4.74878200
H	-4.67420600	4.51830300	6.82779700
H	-3.51141800	9.09966000	-0.38737100
H	-3.22779900	7.40222600	0.01195200
H	-2.98278300	10.23876800	8.10498000
H	-1.57105800	11.25648300	7.87819600
H	-3.80701200	8.86229600	5.67030400
H	0.13133800	10.32236500	5.98283600
H	-0.02557400	8.94726900	3.81753500
H	-1.37526800	9.56717800	8.35316000
H	0.04931000	5.13776100	4.70957900
H	-0.91287500	1.87609500	1.13018300
H	-1.86533600	8.49799400	-0.25833400
O	-5.61233800	7.40683400	2.98278200
H	-4.98360000	8.06772900	2.62122000
H	-6.49669000	7.78676600	2.92276200
O	0.29443300	7.32028300	2.30235600
H	-0.10571300	7.75792600	1.53940100
H	1.16057400	6.99724700	2.02552800
Co	-2.39768900	7.21820900	3.29318100

Cartesian coordinates for the DFT calculation of CuII-NikR, doublet, optimized

structure

C	2.33731200	-0.93001900	1.87816200
N	2.68432900	-1.15743400	3.20543700
C	3.52983200	-0.70646600	1.24470600
C	4.02889200	-1.06296400	3.33708800
N	4.57079000	-0.78981700	2.15872400
C	6.36512900	-2.99214800	-0.88353600
N	6.04588100	-2.61297300	0.42473500
C	5.78390400	-4.20733500	-1.13332900
C	5.30416000	-3.58445800	0.92630300
N	5.12185400	-4.57089800	0.02196400
S	7.26671300	0.96233600	2.99556300
C	10.35478600	-2.53944200	1.16321600
N	10.63964800	-1.18444100	1.11191400
C	9.01584300	-2.60787800	1.40824300
C	9.49763900	-0.49347200	1.33012200
N	8.49100600	-1.33309300	1.50862800



Cu	6.55246300	-0.89435900	1.78896900
H	2.03934400	-1.33396900	3.96195600
H	3.72686000	-0.47707200	0.20914500
H	4.58693300	-1.18165700	4.25983900
H	5.78312100	-4.82950500	-2.01383800
H	4.88099600	-3.60667900	1.91809300
H	4.58795700	-5.41430800	0.16407400
H	11.54941600	-0.77334300	0.96024600
H	8.40114800	-3.48557700	1.51755200
H	9.43311200	0.57965800	1.38219000
C	6.18279900	2.32118800	2.43642200
H	6.34397200	3.17562500	3.09497200
H	6.43617500	2.62891100	1.41781800
H	5.13153900	2.04230800	2.47943500
C	0.92464500	-0.98423800	1.38952000
H	0.48780100	-1.98333500	1.53500400
H	0.28524000	-0.26401400	1.90365000
H	0.88715700	-0.76357600	0.32216600
C	7.20347100	-2.18923700	-1.83496400
H	7.21417000	-2.66605100	-2.81713900
H	6.79758800	-1.17601000	-1.94387600
H	8.23268000	-2.10214600	-1.48263100
C	11.36764500	-3.60403900	0.98401300
H	11.85683100	-3.54253800	0.00408000
H	12.15062000	-3.55975100	1.74573400
H	10.89625400	-4.58397400	1.05292600
O	6.32019800	-1.18026800	5.28923800
H	6.67163700	-0.30675600	5.04666000
H	6.32253800	-1.24601200	6.25110500
O	5.21419600	0.74404800	-1.26152900
H	5.72636400	1.49175600	-0.92928800
H	4.75198300	1.07320300	-2.04421700

Cartesian coordinates for the DFT calculation of CuI-NikR optimized structure

C	2.35976400	-0.90986600	1.80044100
N	2.73333100	-0.38282400	3.03288100
C	3.54279200	-1.26511300	1.21134000
C	4.08452700	-0.42803900	3.13318600
N	4.60466600	-0.96965300	2.04734600
C	6.48383700	-3.37890800	-1.25826500
N	6.08585000	-3.41158800	0.06947900

C	6.08341900	-4.54194600	-1.88109000
C	5.46739500	-4.55803400	0.24329000
N	5.44961100	-5.29190600	-0.90980800
S	7.13788000	1.09505300	3.45880000
C	10.31556900	-2.55507400	1.13363800
N	10.61722900	-1.19611000	1.10712900
C	8.96249200	-2.59973300	1.33106100
C	9.46335600	-0.49506000	1.25078200
N	8.44047400	-1.31670400	1.37311800
Cu	6.55292200	-0.89473600	1.78832200
H	2.11351000	0.00540000	3.72743000
H	3.70014200	-1.76444200	0.26737600
H	4.66690900	-0.03078200	3.95311700
H	6.20314200	-4.88714400	-2.89743600
H	5.04358400	-4.90931300	1.17455600
H	5.05694600	-6.21332500	-1.03068900
H	11.53858800	-0.78717000	1.04978700
H	8.32606500	-3.46668000	1.41113100
H	9.39903900	0.58081700	1.31479000
C	6.18280100	2.32115000	2.43658600
H	5.35134600	1.83735500	1.92111100
H	5.77790400	3.11537900	3.06992000
H	6.84255500	2.79717000	1.70190500
C	0.92481400	-0.98419300	1.38960000
H	0.27380300	-1.07372400	2.26569100
H	0.60293000	-0.09768700	0.82722000
H	0.74155800	-1.85568900	0.75523200
C	7.20330200	-2.18921600	-1.83483900
H	8.12791700	-2.47868300	-2.34650900
H	6.57529600	-1.66669500	-2.56921200
H	7.44184600	-1.47987700	-1.04459200
C	11.36718400	-3.60368900	0.98429200
H	11.88570500	-3.54438700	0.01584000
H	12.13237900	-3.52423200	1.76934000
H	10.92911300	-4.60223400	1.06078000
O	7.02457700	-2.27009200	4.27587800
H	7.17909000	-1.32506100	4.43456800
H	7.15124600	-2.78606200	5.07766700
O	6.26294200	0.83235300	-0.54514600
H	6.61786500	1.65135500	-0.18648700
H	5.84421500	1.01548900	-1.39085900