ELECTRONIC SUPPLEMENTARY INFORMATION

Introducing the penicillamine moiety into a metallopeptide mimicking the NiSOD enzyme: electronic and kinetic effects

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Experimental Section

Materials. The peptide used in this study was purchased from Synpeptide Co. (Shanghai, China) and used without further purification. The concentration of the peptide stock solution (ca. 4 mM) was determined by pH-potentiometric titrations. According to these titrations, the peptide contains small amounts of trifluoro acetate which was used to cleavage the resin and the protecting groups during the preparation of the peptide. This contaminant has negligible effect on the complexation processes.

The $NiCl_2$ stock solution was prepared from the highest available grade (≥ 99.95 %; VWR Int., USA) and its concentration was checked by complexometric titration using EDTA. In all experiments, doubly-deionized and ultrafiltered water (ELGA Purelab Classic system) was used.

pH potentiometry. The protonation constants ($\log K_i$) of the ligands and the overall stability constants ($\log \beta_{pqr}$) were determined by pH-potentiometric titration method using carbonate ion free KOH solution. The carbonate contamination (less than 0.10 %) was determined using the appropriate Gran functions.[1] In these titrations, 3 mL aliquots of the ligands (ca. 2.0 mM) were titrated either in the absence and the presence of metal ion at 1:1 ratio and 1:2 ratios (I = 0.2 M using KCl, T = 298 K). The headspace over the sample was purged with argon to ensure the absence of oxygen and carbon dioxide. The samples were stirred using a VELP scientific magnetic stirrer and the pH measurements were made using a MOLSPIN pH-meter equipped with a 6.0234.110 combined glass electrode (Metrohm) and a MOL-ACS microburette. The system was considered to be in equilibrium when the measured potential remained constant within a 0.03 mV range for 9 s. The pH reading was converted to hydrogen ion concentration as described by Irving et al.[2] Protonation constants and the overall stability constants, $\beta_{pqr} = [Ni_pH_qL_r]/[Ni]^p[H]^q[L]^r$ of the nickel(II) complexes were calculated by using the designated computational programs, SUPERQUAD[3] and PSEQUAD.[4] The PSEQUEAD program was also used to calculate the individual UV-vis spectra of the ligand. The concentration distribution curves of the complexes formed between nickel(II) and **wtPen** were calculated by using the computational program, MEDUSA.[5]

Spectroscopic methods. UV-visible spectra of the nickel(II) complexes were recorded with an Agilent Technologies Cary 60 UV-VIS spectrophotometer in the 200 –800 nm wavelength range using the same concentration range as in the pH-potentiometric titrations. The circular dichroism spectra were registered with a Jasco J-810 spectropolarimeter using 1 mm and/or 1 cm cells in the 250 – 800 nm wavelength range. The individual spectra of the complexes were

calculated by solving the overdetermined linear equation system with Matlab on the basis of the estimated stability constants.[6]

All CW-EPR spectra were recorded with a BRUKER EleXsys E500 spectrometer (microwave frequency 9.45 GHz, microwave power 13 mW, modulation amplitude 5 G, modulation frequency 100 kHz). An 0.2 mL aliquot of Ni(II) sample solution was introduced into a quartz EPR tube then 0.1 mL DMSO solution containing KO_2 and 18-crown-6 (Acros Organics) was added for *in situ* oxidation. Frozen solution EPR spectra were measured in a Dewar container filled with liquid nitrogen at 77 K. The background of the spectrum was taken into account by fitting a singlet component EPR spectrum in order to accurately describe the spectrum of the Ni(III) component. The measured spectra were simulated using the EPR program designated by Rockenbauer and Korecz.[7] Rhombic ***g***-tensor have been used for the simulation of the components. Orientation dependent linewidths were considered. The nitrogen coupling constants and the linewidth parameters were obtained in field units (1Gauss = 10^{-4} T).

ESI-TOF-MS measurements were made with a Bruker maXis II MicroTOF-Q type Qq-TOF-MS instrument (Bruker Daltonik, Bremen, Germany) in negative mode. The instrument was equipped with an electrospray ion source where the spray voltage was 4 kV. N_2 was utilized as a drying gas and the drying temperature was 200 °C. The spectra were accumulated and recorded using a digitalizer at a sampling rate of 2 GHz. The mass spectra were calibrated externally using the exact masses of sodium formate clusters. The spectra were evaluated using DataAnalysis 4.4 software from Bruker. The isotopic patterns of the complexes were calculated using the IsotopePattern software from Bruker.

1D ^{1}H and 2D (^{1}H–^{13}C HSQC) NMR spectra were recorded on a Bruker Avance I 400 spectrometer equipped a BB inverse *z* gradient probe at 298 K. The chemical shifts were referenced to sodium 3-(trimethylsilyl)-1-propane sulfonate (TSP, δ_{TSP} = 0.00 ppm) dissolved in the sample and D_2O was used as a solvent. The HSQC spectra were collected by using gradient pulses in the *z* direction with the standard Bruker pulse sequence.

In the MS and spectrophotometric measurements, the samples were freshly prepared and purged with argon, and the pH was adjusted immediately before the samples were introduced into the ESI-source or transferred into the cuvettes.

Cyclic voltammetry and differential pulse voltammetry. Electrochemical measurements (cyclic voltammetry (CV) and differential pulse voltammetry (DPV)) were performed using a BASI Epsilon Eclipse potentiostat (Bioanalytical Systems Inc., West Lafayette, USA) equipped with a three-electrode arrangement that consists of a platinum wire auxiliary

electrode (ALS Co. Japan), a glassy carbon electrode (CHI104) and a Ag/AgCl/3 M KCl reference electrode. The electrochemical measurements were carried out in 0.1 M $NaClO_4$ at 25 °C. Aqueous solution of $K_3[Fe(CN)_6]$ was used to calibrate the system. The samples were degassed before the measurements using argon gas. The concentration of the samples was 2 mM and the pH was adjusted to 7.6 by adding of NaOH solution. For the CV measurements, the voltage range was varied between – 400 mV – 1200 mV with the sweep rate of 50 mVs^{-1}. For the DPV measurements, the experimental conditions were as follows: voltage range: – 400 mV – 900 mV, pulse width: 50 ms, pulse period: 200 ms and pulse amplitude: 50 mV.

Stopped flow measurements. The catalytic activities of the Ni(II) complexes in the decomposition of O_2^- and the formation of Ni(III) transient species and further nickel complexes were studied using an Applied Photophysics SX-20 stopped-flow instrument equipped with a photomultiplier tube as the detector. The kinetic traces were collected using 2- or 10 mm optical path length at 25 °C. The measurements were carried out in 1:1 DMSO − water mixture, and the instrument was used in sequential mode to circumvent the relatively slow homogenization of the solvent mixture. Preliminary observations confirmed that mixing water with DMSO is not instantaneous in a conventional stopped flow experiment, i.e., the spectral disturbances fade away several ten milliseconds after mixing. This artifact was avoided by using the sequential stopped-flow method.[8] The first syringe was filled with water, the second one with KO_2 in DMSO, while the third one with the complex dissolved in 1:1 DMSO and aqueous HEPES buffer (50 mM, pH 7.6). In the first phase of these experiments, the aging loop was filled with the 1:1 mixture of the first and second solutions to produce a KO_2 reagent in 1:1 water – DMSO solvent. After 40 s incubation time, this mixture was reacted with the solution in the third syringe and the progress of the reaction was monitored at 260 or 376 nm. To study the formation of Ni(III) species, the same experimental protocol was used but the instrument was equipped with a PDA detector.

The O_2^- solutions were freshly prepared before each experiment by dissolving solid KO_2 (Acros Organics) in vigorously stirred DMSO containing 18-crown-6 (Sigma-Aldrich). The formation of the ion pair between O_2^- and K^+ incorporated in the crown ether improves the solubility of KO_2. Noticeably, this carrier molecule does not affect the kinetic experiments. The concentration of the superoxide stock solution was determined by stopped-flow method. In the absence of the catalyst, the initial absorbance values were used to determine the concentration using the molar absorbance of superoxide anion at 260 nm, $\varepsilon_{O_2^-} = 2686\ M^{-1}\ cm^{-1}$.[8]

Computational methods. Molecular Dynamics (MD) simulations were set up with the *xleap*, solvating the structures with a box of pre-equilibrated TIP3P water molecules and the total charge was balanced with Na^+ ions (*ions94.lib* library). The AMBER14SB force field[9] was used for the standard residues, while the GAFF force field was adopted for the remaining atoms. Ni-bonding force constants and equilibrium parameters were obtained through the Seminario method, using Gaussian 16[10] to compute the geometry and harmonic frequencies at DFT level with the B3LYP[11] functional combined with scalar-relativistic Stuttgart−Dresden SDD pseudopotential and its associated double-ζ basis set plus *f* polarization functions[12] for Ni. The 6-31g(d,p) basis set was used for H, C, N, O and S. All calculations accounted for solvent effect using the continuum model for water.[13] Point charges were derived using the RESP (Restrained ElectroStatic Potential) model.[14] The force field building operations were carried out using the MCPB.py.[15] The solvent and the whole system were sequentially submitted to 3000 energy minimization steps to relax possible steric clashes. Then, thermalization of water molecules and side chains was achieved by increasing the temperature from 100 K up to 300 K. MD simulations under periodic boundary conditions were carried out during 200 ns with OpenMM engine[16] through OMMProtocol.[17] The trajectories convergence was assessed by RMSI, RMSF, Counting Clustering Method and PCA analysis, considering the full exploration of the conformational space as a criterion of convergence.[18] The QT clustering method was used to generate clusters of the most sampled conformations for each trajectory,[19] taking the RMSD between frames as distance metric. The central structure of the most populated cluster for each variant was used in the further DFT studies.

Optimizations of the Ni(II)/Ni(III)–**wtSOD** and Ni(II)/Ni(III)–**wtPen** metallopeptides were computed through Gaussian 16 using the B97D functional combined with scalar-relativistic Stuttgart-Dresden SDD pseudopotential and double-ζ basis plus a set of *f* polarization functions[12] for Ni. The 6-31g(d,p) basis set was used for H, C, N, O and S. All calculations accounted for solvent effect using the continuum model for water.[13]

UV-vis vertical excitations were simulated on the Time-dependent density functional theory (TD-DFT) framework in solvent continuum model.[20] The simulations were carried out on the previously optimized geometries in solvent (water) using HSE06 functional and the triple-ζ type *def2*-TZVP basis set, according to the method established previously.[21] The predicted electronic spectra were generated using Gabedit software,[22] and the molecular orbitals (MOs) involved in the transitions were simulated performing a Mulliken population analysis (MPA)

with Gaussian 16 at the same level of theory used for the TD-DFT calculations and identified *via* the AOMix package (vers. 6.52).[23]

The ***g*** and ***A*** tensors of ^{63}Ni and ^{14}N nuclei were computed for each structure using the method implemented into the ORCA package (vers, 4.0),[24, 25] using the functional BP coupled with a triple-ζ basis set 6-311g(d,p). BP gives good results in the prediction of spin Hamiltonian parameters of Ni(III) complexes,[26] as was confirmed in a small benchmark for well characterized species such as $[Ni^{III}(mnt)_2]^-$, $[Ni^{III}(salophCl_2)]^+$, $[Ni^{III}(salophCl_2)(py)]^+$ and $[Ni^{III}(salophCl_2)(py)_2]^+$ – where mnt(2–), salophCl$_2$(2–) and py are maleonitriledithiolato, *N*,*N*'-disalicylidene-4,5-dichloro-1,2-phenylenediamine and pyridine ligands–, using three different functionals, B3LYP, PBE0 and BP (see Table S8 and the Cartesian coordinates in Table S9-S12). EPR parameters were taken from refs. [27] [28] [29].

Acid-base properties

In accordance with the structure of the peptide, the terminal amino group, the imidazole-*N* of histidine, the carboxylate residue of aspartic acid, the hydroxyl group of tyrosine as well as the two thiolate groups of penicillamine and cysteine are taking part in acid-base processes. Some of the stepwise acid-base processes significantly overlap, however the fitting of the titration curve reveals that 6 acid dissociation constants can be estimated in agreement with the expected number of acid-base processes. Earlier studies on similar systems[30, 31,32] and thorough analysis of the data confirm that the lowest log K_i value is assigned to the carboxylate group of aspartic acid, while the highest log K_i belongs to the hydroxyl function of tyrosine moiety. The second deprotonation step occurs on the imidazole-*N* of histidine with increased acidity. This effect can readily be explained by the intramolecular hydrogen bond between the terminal amino group and the imidazole-*N*. Such a feature has already been reported for several *N*-terminally free peptides containing histidine in the first position.[33,34] The further deprotonation processes (deprotonations of the two thiols, *N*-terminal ammonium functions and the phenolate group of tyrosine moiety) significantly overlap. On the basis of plausible considerations and literature data, it is reasonable to assume that the subsequent deprotonation step can be mainly attributed to the thiolate group of penicillamine. Earlier studies demonstrated that the insertion of the penicillamine into the peptide chain significantly enhances the acidity of the thiolate group which is due to the presence of the methyl substituents on the β-carbon atom.[35] The same features apply in our system. The overall cumulative basicity of **wtPen** is somewhat higher than that of **wtSOD**, however the

replacement of the cysteine moiety with penicillamine does not have significant effect on this feature.

The protonation equilibria were also studied by UV-vis spectroscopy and the spectra are reported in Figure S2. UV-vis spectra recorded in acidic conditions exhibit a dominant transition at 275 nm. Upon increasing the pH, the spectra show a new absorption band at 291 nm. This band mainly belongs to the absorption of the deprotonated phenolic side chain of tyrosine. The absorptions at 291 nm were fitted as a function of pH and excellent agreement was found between the corresponding log K_i values obtained from pH-potentiometry and UV-vis spectroscopy; 10.07 ± 0.05 *vs.* 9.92 ± 0.02 (Figure S3). This result confirms that the highest log K_i belongs to the hydroxyl function of tyrosine moiety. In addition, the individual spectra of the corresponding species were also calculated and are reported in Figure S4.

Table S1. The formation constants (log β_i) of the peptide and the stability constants (logβ_{pqr}) of the complexes formed between nickel(II) and **wtPen**.[a]

log β_i	**wtPen**	**wtSOD**[b]	log β_{pqr}	**wtPen**	**wtSOD**[b]
Species			Species		
$[H_6L]^{2+}$	43.77(5)	43.31	$[NiH_3L]^{+}$	33.41(2)	33.44
$[H_5L]^{+}$	39.99(7)	39.73	$[NiHL]^{-}$	22.61(1)	22.22
$[H_4L]$	34.57(6)	34.25	$[NiL]^{2-}$	15.75(3)	15.71
$[H_3L]^{-}$	27.48(6)	27.05	$[NiH_{-1}L]^{3-}$	5.86(4)	6.45
$[H_2L]^{2-}$	19.22(6)	18.80	$[NiH_{-2}L]^{4-}$	-5.35(5)	
$[HL]^{3-}$	10.07(5)	9.88			
Σlog K_i	43.77	43.31	log $K(N^-)$[c]	6.86	6.52
Fitted pH range	2.6 – 11.6		Fitted pH range	3.9 – 11.3	

[a] 3σ standard deviations are indicated in parentheses. I = 0.2 M KCl, T =298 K. [b] Data are taken from ref. [31]. [c] Equilibrium constant for the deprotonation of amide N. log $K(N^-)$ = log β(NiHL) – log β(NiL).

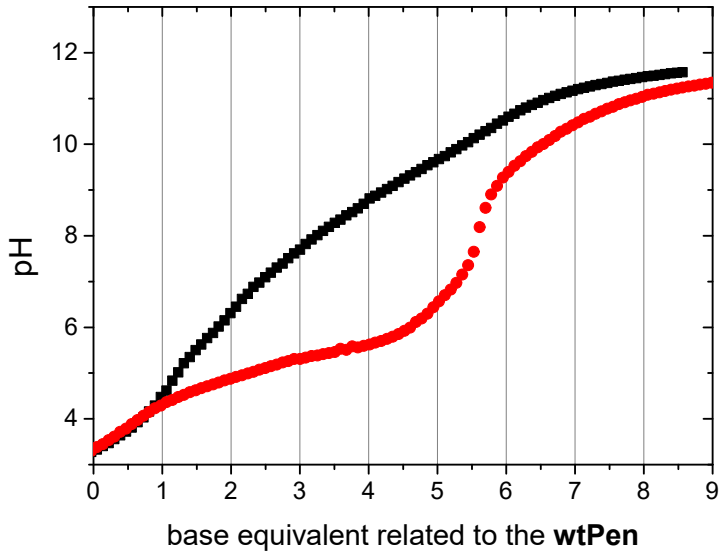

Figure S1. Representative titration curves of the H^+/**wtPen** (black) and Ni(II)/**wtPen** (red) systems at 0.9:1 metal to ligand ratio. I = 0.2 M KCl, T = 25 °C, $c_{\mathbf{wtPen}}$ = 2 mM

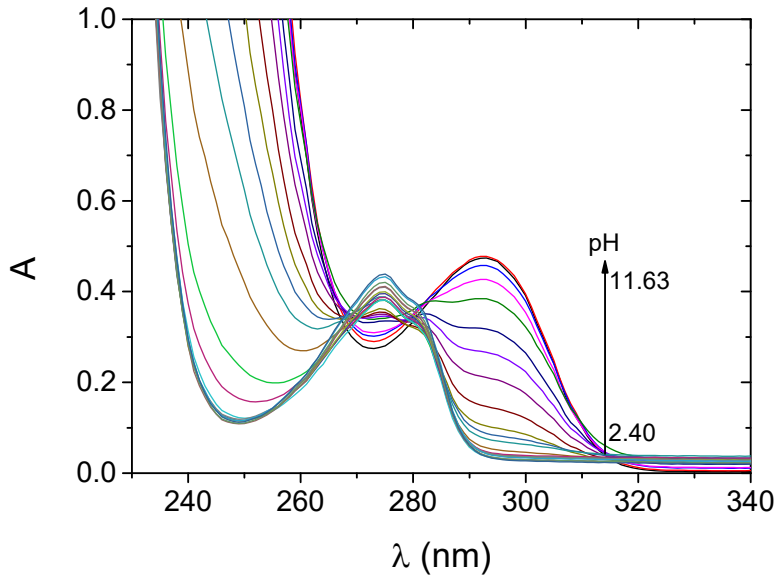

Figure S2. pH-dependent UV-vis spectra recorded in the H^+/**wtPen** system. l = 2mm, I = 0.2 M KCl, T = 25 °C, $c_{\mathbf{wtPen}}$ = 1 mM

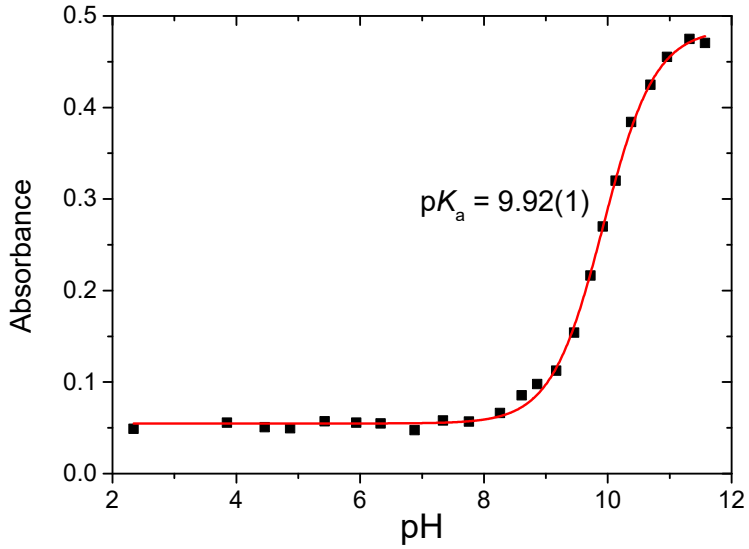

Figure S3. Experimental (squares) and fitted (solid line) absorbances at 291 nm as a function of pH recorded in the H^+/**wtPen** system. l = 2mm, I = 0.2 M KCl, T = 25 °C, $c_{\mathbf{wtPen}}$ = 1 mM

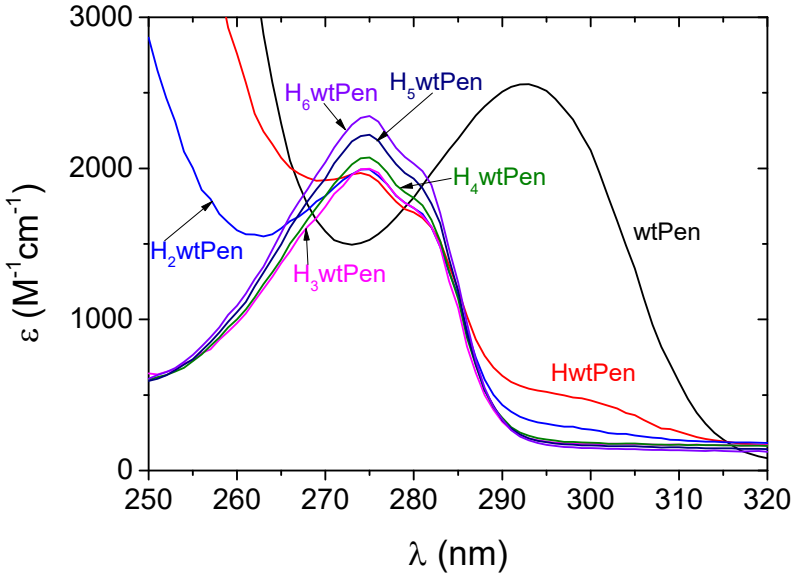

Figure S4. Calculated individual spectra of the different protonation forms of **wtPen**.

Nickel(II) complexes.

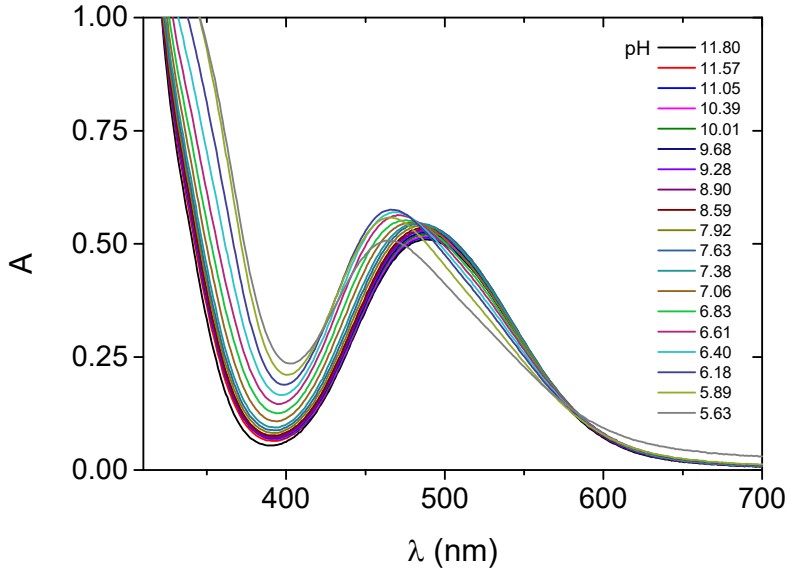

Figure S5. pH-dependent UV-vis spectra recorded in the Ni(II)/wtPen system at 0.9:1 metal to ligand ratio. l = 10 mm, I = 0.2 M KCl, T = 25 °C, $c_{\mathbf{wtPen}}$ = 2 mM

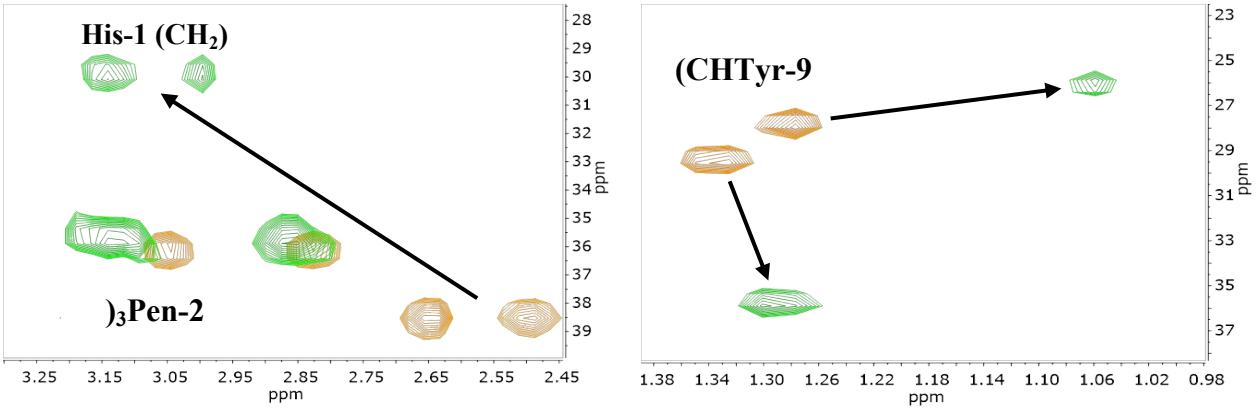

Figure S6. Selected parts of the ^{1}H–^{13}C HSQC spectra recorded in the H^{+}/**wtPen** (orange) and Ni(II)/**wtPen** system at 1:1 metal to ligand ratio at pH 7.8. $c_{\mathbf{wtPen}}$ = 5 mM.

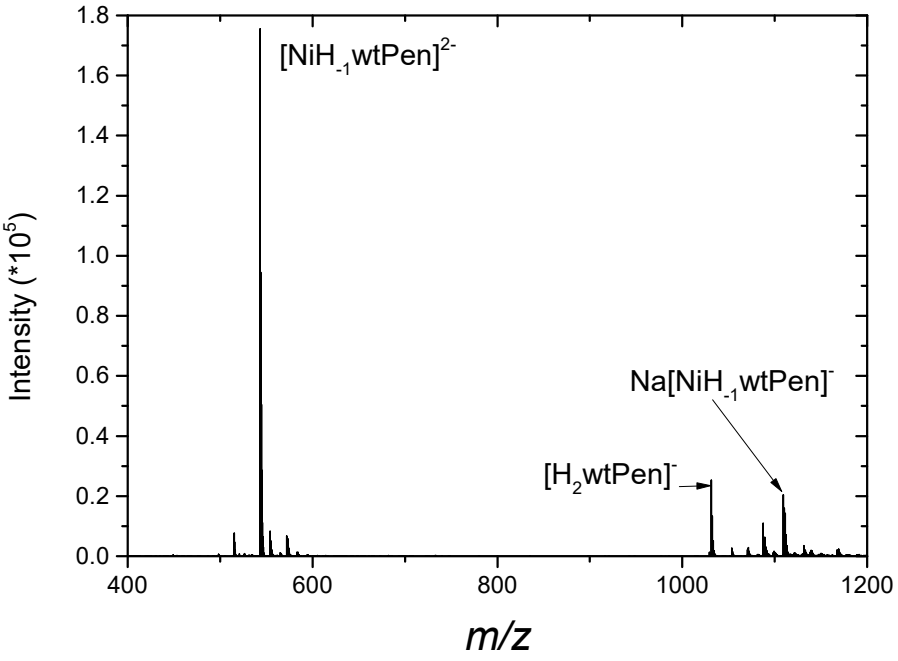

Figure S7. ESI-TOF-MS spectra recorded in the Ni(II)/**wtPen** 0.9:1 system at pH 8. $c_{\mathbf{wtPen}}$ = 0.1 mM.

Table S2. The results of ESI-TOF-MS experiments: measured and calculated *m/z* values obtained for the Ni(II)/**wtPen** 1:1 system. L refers to **wtPen**.

Species : Stoichiometry	*m/z* observed	*m/z* calculated
$[\mathbf{L}+3H^+]^-$: $C_{45}H_{67}N_{12}O_{12}S_2$	1031.4450	1031.4448
$[\mathbf{L}+2H^++Na^+]^-$: $NaC_{45}H_{66}N_{12}O_{12}S_2$	1053.4273	1053.4268
$[\mathbf{L}+2H^+]^{2-}$: $C_{45}H_{66}N_{12}O_{12}S_2$	512.2191	515.2188
$[NiH_{-1}\mathbf{L}+H^+]^{2-}$: $NiC_{45}H_{64}N_{12}O_{12}S_2$	543.1789	543.1786
$[NiH_{-1}\mathbf{L}+Na^+]^{2-}$: $NaNiC_{45}H_{63}N_{12}O_{12}S_2$	554.1699	554.1696
$[NiH_{-1}\mathbf{L}+H^++Na^+]^-$: $NaNiC_{45}H_{64}N_{12}O_{12}S_2$	1109.3469	1109.3465

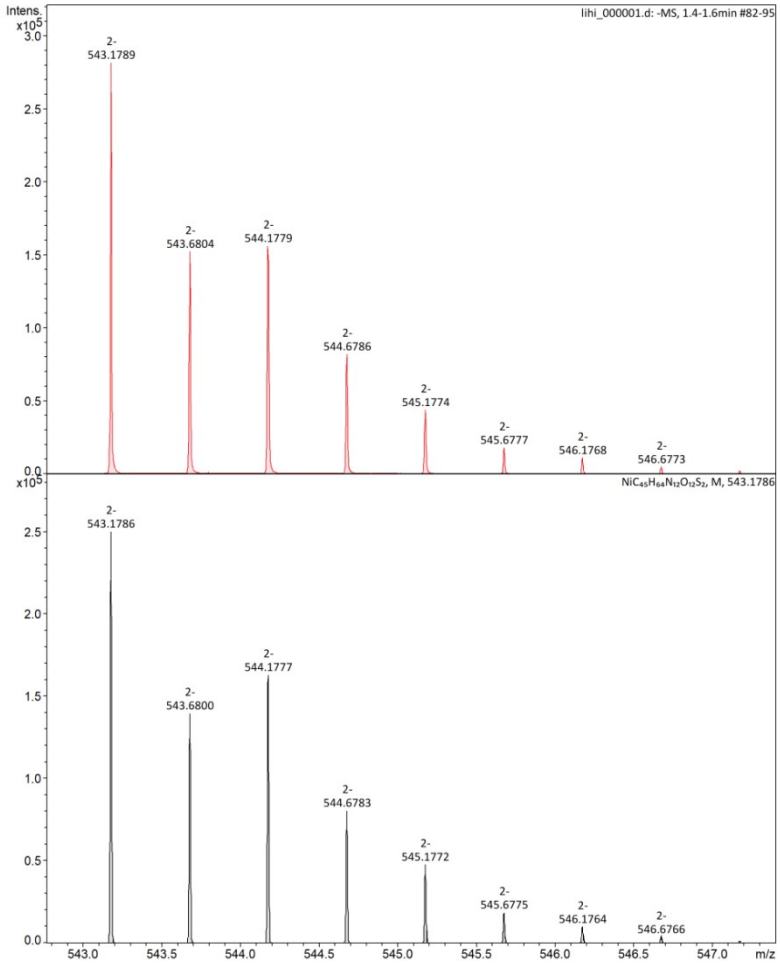

Figure S8. Experimental (top) and calculated isotopic patterns of the $[NiH_{-1}L]^{2-}$ species (bottom), L refers to **wtPen**.

Complex formation equilibria of $[NiH_{-1}L]^{3-}$ and $[NiH_{-2}L]^{4-}$ complexes.

The deprotonation of non-coordinating tyrosine residue yields the $[NiH_{-1}L]^{3-}$ complex. Neither the CD nor the UV-vis spectra exhibit significant changes reflecting that the coordination sphere remains intact, and the tyrosine residue does not have any contribution to the metal binding. This is also confirmed by the calculated individual spectra (Figure S9). The corresponding deprotonation constant, log K = 9.89, is close to the log K_i of the side chain of tyrosyl-OH group in the free ligand (log K_i = 10.07). This result is also consistent with the conclusion that the tyrosine moiety is not involved in the metal binding. In strongly alkaline solution, a further base consumption process yields the $[NiH_{-2}L]^{4-}$ complex. Although, the formation of this complex is accompanied with moderate spectral changes, the binding of the OH^- group i.e., formation of mixed hydroxide species, is unlikely. According to earlier literature data, the reorganization of the coordination sphere occurs, and a further amide nitrogen is involved in the metal binding.[34] Consequently, nickel(II) is accommodated by the (NH_2,N^-,N^-,S^-_{Cys6}) donor set and the thiolate group of penicillamine does not coordinate to the metal ion.

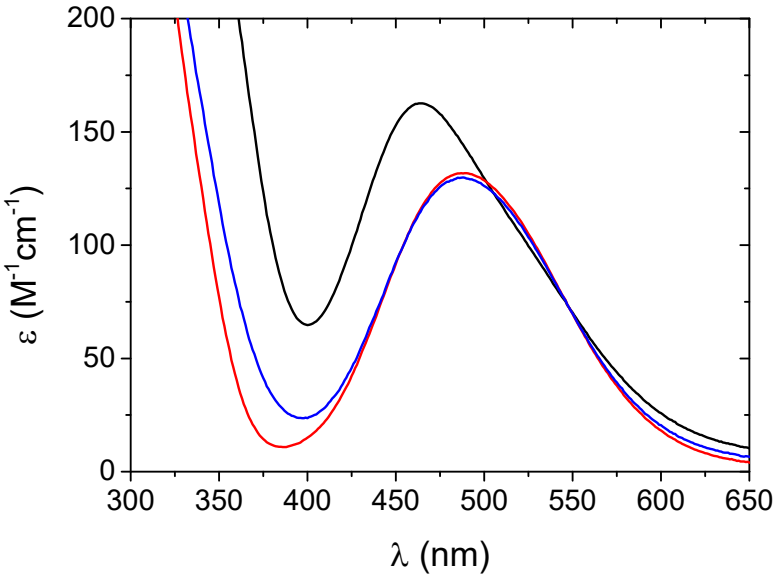

Figure S9. Calculated individual spectra of the complexes formed in the Ni(II)/**wtPen** system (black: NiHL; red: NiL; blue: $NiH_{-1}L$).

Analysis of the vertical electronic transitions of Ni(II)/wtPen and Ni(II)/wtSOD.

In the first of these transition, one electron is promoted from an internal MO with Ni-d_{yz} character to an unoccupied MOs mainly localised on the Pro5 residue. The next transitions are LMCT, in which the promotion occurs between an internal occupied MO highly localized on the (NH_{2His1},N^-_{His1},S^-_{Cys6}) coordinating set toward the Ni-$d_{x^2-y^2}$ based LUMO orbital. Other less intense MLCT and LMCT transitions involve excitations with main Ni-$d_{xz/yz/z^2}$ → $L_{Tyr8/Cys6/His1/Ala7}$ or L_{Asp3} → Ni-$d_{x^2-y^2}$ character (see Table S5). Globally, the characterized transitions account for the experimental UV-vis and CD observations confirming both the coordination mode and the folding state of the Ni(II)–**wtPen** metallopeptide. For the sake of completeness, the electronic vertical transitions of Ni(II)–**wtSOD** metallopeptide have been also characterized, obtaining similar results that confirm the (NH_{2His1},N^-_{His1},S^-_{Cys6}) coordination mode (Table S6).

Table S3. Cartesian coordinates of the optimized structure of Ni^{II}/**wtSOD** complex.

N	-4.510422000	-0.936432000	-1.640376000
C	-5.907358000	-0.409274000	-1.670270000
C	-6.005863000	0.675475000	-0.581066000
O	-6.864958000	1.574660000	-0.631521000
C	-6.965285000	-1.526212000	-1.459157000
C	-6.948939000	-2.119618000	-0.078142000
N	-7.813827000	-1.671085000	0.909112000
C	-6.032123000	-3.007042000	0.455809000
C	-7.411160000	-2.262001000	2.023608000
N	-6.345598000	-3.096928000	1.797847000
H	-6.089879000	0.078859000	-2.639318000
H	-7.949398000	-1.069384000	-1.632546000
H	-6.810257000	-2.302435000	-2.229957000

H	-5.169630000	-3.513922000	0.042571000
H	-7.864567000	-2.156837000	3.005300000
H	-3.933013000	-0.235512000	-2.161385000
H	-4.446463000	-1.836380000	-2.122167000
H	-5.778193000	-3.560226000	2.495254000
N	-5.077280000	0.484780000	0.392287000
C	-4.898781000	1.546721000	1.378715000
C	-3.949156000	2.666637000	0.867464000
O	-3.943339000	3.801970000	1.361714000
C	-4.367641000	0.899766000	2.667073000
S	-3.082857000	-0.387316000	2.262343000
H	-5.856973000	2.051553000	1.574964000
H	-3.935696000	1.656573000	3.340018000
H	-5.206121000	0.401454000	3.175640000
N	-3.085115000	2.242877000	-0.102245000
H	-3.307806000	1.343651000	-0.525991000
C	-2.291260000	3.086334000	-0.985973000
H	-1.647684000	2.366004000	-1.509183000
C	-3.145679000	3.647370000	-2.122668000
H	-2.527972000	4.304415000	-2.755687000
H	-3.984934000	4.240578000	-1.733783000
C	-3.728209000	2.456207000	-3.002714000
O	-4.641802000	2.750635000	-3.798436000
O	-3.188140000	1.295946000	-2.817443000
C	-1.218881000	3.927512000	-0.273271000
O	-0.582734000	4.813255000	-0.851967000
N	-0.870461000	3.415112000	0.963666000
H	-1.499471000	2.691426000	1.298627000
C	0.502874000	3.310963000	1.473209000
H	0.822201000	4.259447000	1.926978000
C	0.491452000	2.198314000	2.557546000
H	-0.024794000	2.609147000	3.441941000
H	-0.130571000	1.361139000	2.202529000
C	1.853176000	1.621423000	2.981674000
H	2.292296000	1.138593000	2.096292000
C	2.825650000	2.700189000	3.486528000
H	2.399515000	3.212371000	4.366283000
H	3.030428000	3.445029000	2.705896000
H	3.781853000	2.244222000	3.785248000
C	1.622651000	0.525720000	4.038152000
H	1.212580000	0.970046000	4.961149000
H	0.909547000	-0.225750000	3.668860000
H	2.556877000	0.001937000	4.281389000
C	1.550191000	3.102102000	0.342781000
O	2.533275000	3.855273000	0.273013000
N	1.333214000	2.122473000	-0.591440000
C	1.977526000	2.194589000	-1.912233000
H	2.817055000	1.488317000	-1.974443000
H	2.350469000	3.212213000	-2.072393000
C	0.828890000	1.779887000	-2.844346000
H	0.142615000	2.629770000	-2.969791000
H	1.182278000	1.450812000	-3.831728000
C	0.131716000	0.647212000	-2.062361000
H	0.624987000	-0.311807000	-2.280616000
H	-0.939236000	0.564804000	-2.292815000

C	0.358056000	1.029459000	-0.553095000
H	-0.576379000	1.342463000	-0.081260000
C	0.890174000	-0.219474000	0.155935000
O	2.098648000	-0.529682000	0.127075000
N	-0.079470000	-1.005459000	0.659289000
C	0.088827000	-2.417157000	1.017698000
C	0.849659000	-3.227748000	-0.054990000
O	1.630069000	-4.138499000	0.243375000
C	-1.321075000	-3.049031000	1.238841000
S	-2.529001000	-2.749452000	-0.136430000
H	-1.043396000	-0.655290000	0.639005000
H	0.689509000	-2.509569000	1.934813000
H	-1.743124000	-2.653945000	2.173085000
H	-1.175925000	-4.132676000	1.356895000
N	0.554127000	-2.891526000	-1.351214000
H	-0.324830000	-2.389077000	-1.488963000
C	1.136414000	-3.636075000	-2.457537000
H	1.082621000	-4.719831000	-2.276100000
H	0.564304000	-3.408030000	-3.367028000
C	2.629668000	-3.338180000	-2.744536000
O	3.249466000	-4.054320000	-3.536374000
N	3.147597000	-2.251504000	-2.100808000
H	2.568697000	-1.771512000	-1.411826000
C	4.578756000	-1.941849000	-2.084875000
H	5.055568000	-2.583510000	-2.835812000
C	4.841498000	-0.447638000	-2.406823000
H	4.331666000	0.148336000	-1.634197000
C	6.344201000	-0.128432000	-2.323231000
H	6.522342000	0.929062000	-2.564943000
H	6.734442000	-0.307032000	-1.312479000
H	6.909577000	-0.748688000	-3.038089000
C	4.265388000	-0.075347000	-3.782545000
H	4.776913000	-0.640930000	-4.578055000
H	3.191627000	-0.303496000	-3.837218000
H	4.406354000	0.998506000	-3.978648000
C	5.162729000	-2.351061000	-0.707998000
O	5.980441000	-3.276851000	-0.573503000
N	4.697853000	-1.598400000	0.322238000
H	3.890176000	-0.995740000	0.175684000
C	5.081228000	-1.790616000	1.718269000
H	6.081147000	-2.248335000	1.706560000
C	5.090842000	-0.428640000	2.449704000
H	4.047592000	-0.156263000	2.652405000
H	5.582150000	-0.570047000	3.424623000
C	5.766035000	0.659784000	1.640782000
C	7.168081000	0.767199000	1.564776000
H	7.790830000	0.082227000	2.145320000
C	7.782665000	1.731336000	0.753993000
H	8.868312000	1.811542000	0.693247000
C	6.987597000	2.616129000	0.000997000
O	7.635589000	3.542239000	-0.786785000
H	6.959464000	4.075682000	-1.232859000
C	5.586088000	2.532326000	0.071525000
H	4.944158000	3.227189000	-0.474334000
C	4.992927000	1.554401000	0.877994000

H	3.907617000	1.491622000	0.898693000
C	4.056276000	-2.786928000	2.337811000
O	3.176592000	-2.443099000	3.130287000
N	4.202455000	-4.070894000	1.872906000
H	4.803431000	-4.189594000	1.057931000
H	3.332880000	-4.596557000	1.845359000
Ni	-3.808691000	-0.923929000	0.241565000

Table S4. Cartesian coordinates of the optimized structure of Ni^{II}/**wtPen** complex.

N	1.117410000	1.151788000	0.972827000
C	0.255225000	1.844385000	1.976427000
C	-1.048154000	2.324354000	1.312139000
O	-1.868412000	2.999912000	1.992744000
C	0.964768000	3.061618000	2.631350000
C	1.349153000	4.054587000	1.573400000
N	2.525829000	3.905118000	0.852335000
C	0.576414000	5.055742000	1.017187000
C	2.470552000	4.806022000	-0.118896000
N	1.313352000	5.534689000	-0.051595000
H	0.001223000	1.113098000	2.756315000
H	0.247877000	3.502343000	3.336125000
H	1.855463000	2.722107000	3.180836000
H	-0.422721000	5.403026000	1.246766000
H	3.229215000	4.975982000	-0.876100000
H	1.553294000	0.332345000	1.403494000
H	1.877401000	1.781953000	0.690047000
H	1.014218000	6.246795000	-0.704987000
N	-1.158365000	1.971066000	0.022220000
C	-2.321102000	2.462819000	-0.750586000
C	-3.559905000	1.562889000	-0.511470000
O	-4.002951000	0.750689000	-1.350732000
C	-1.871209000	2.635065000	-2.217421000
S	-0.866457000	1.116199000	-2.688910000
H	-2.617916000	3.453139000	-0.366534000
C	-3.044888000	2.848770000	-3.194192000
C	-0.945549000	3.873334000	-2.259502000
H	-3.758629000	3.561497000	-2.751541000
H	-3.580857000	1.911532000	-3.371673000
H	-2.661449000	3.242243000	-4.150096000
H	-0.122375000	3.758364000	-1.542524000
H	-0.526978000	3.995006000	-3.269411000
H	-1.525970000	4.778853000	-2.002446000
N	-4.104847000	1.733517000	0.726777000
H	-3.612414000	2.420937000	1.304289000
C	-5.541057000	1.540397000	1.050565000
H	-5.698812000	2.058330000	2.003267000
C	-6.428230000	2.251829000	0.005599000
H	-7.476342000	2.127814000	0.324196000
H	-6.284825000	1.789474000	-0.980353000
C	-6.035253000	3.788069000	-0.000568000
O	-5.357787000	4.187626000	-0.994315000
O	-6.403685000	4.425950000	1.025704000
C	-5.921964000	0.065934000	1.308517000

O	-6.472592000	-0.297185000	2.358349000
N	-5.626319000	-0.778799000	0.278531000
H	-5.124074000	-0.359717000	-0.518309000
C	-5.706399000	-2.228737000	0.396196000
H	-6.740425000	-2.519449000	0.637670000
C	-5.288170000	-2.892721000	-0.936362000
H	-4.393399000	-2.384849000	-1.330207000
H	-4.986856000	-3.928942000	-0.724934000
C	-6.381997000	-2.901487000	-2.027163000
H	-7.271830000	-3.399315000	-1.600082000
C	-6.789743000	-1.486516000	-2.482780000
H	-7.511101000	-1.544069000	-3.314461000
H	-5.905914000	-0.926622000	-2.826861000
H	-7.240646000	-0.912015000	-1.663307000
C	-5.897632000	-3.731255000	-3.231613000
H	-5.006062000	-3.263849000	-3.680443000
H	-5.626403000	-4.754904000	-2.928656000
H	-6.675658000	-3.792169000	-4.009078000
C	-4.896449000	-2.801597000	1.595977000
O	-5.406658000	-3.648954000	2.340834000
N	-3.633528000	-2.322775000	1.813527000
C	-2.877285000	-2.793456000	2.990378000
H	-2.803403000	-3.890097000	2.979045000
H	-3.421771000	-2.498196000	3.900095000
C	-1.494258000	-2.103315000	2.862361000
H	-1.123696000	-1.725872000	3.825432000
H	-0.761461000	-2.821376000	2.467770000
C	-1.724890000	-0.983667000	1.824208000
H	-0.820036000	-0.664278000	1.293015000
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C	-2.752803000	-1.635023000	0.872815000
H	-3.279653000	-0.883199000	0.285277000
C	-2.046899000	-2.650557000	-0.067930000
O	-2.187304000	-3.874626000	0.032470000
N	-1.189986000	-2.059505000	-0.950289000
C	-0.213605000	-2.818678000	-1.719388000
C	0.616891000	-3.800241000	-0.861573000
O	1.018334000	-4.874275000	-1.318839000
C	0.741511000	-1.865211000	-2.496564000
S	1.684832000	-0.623402000	-1.492158000
H	-1.163588000	-1.036875000	-1.028666000
H	-0.719409000	-3.458301000	-2.460419000
H	0.150800000	-1.325466000	-3.248824000
H	1.471819000	-2.499974000	-3.019901000
N	0.940308000	-3.346592000	0.391134000
H	0.732646000	-2.375275000	0.599903000
C	1.850926000	-4.076988000	1.250318000
H	1.691786000	-3.762319000	2.290737000
H	1.623538000	-5.148218000	1.170842000
C	3.361247000	-3.916259000	0.964111000
O	4.187205000	-4.499109000	1.674610000
N	3.691070000	-3.109267000	-0.085896000
H	2.958625000	-2.549202000	-0.529987000
C	5.072354000	-2.683050000	-0.298543000
H	5.725816000	-3.559000000	-0.187986000

C	5.233970000	-2.076135000	-1.719502000
H	4.586763000	-1.186217000	-1.769624000
C	6.688243000	-1.647116000	-1.980429000
H	7.352507000	-2.526983000	-1.958410000
H	6.766622000	-1.176719000	-2.971525000
H	7.041891000	-0.930318000	-1.230797000
C	4.768888000	-3.082044000	-2.790414000
H	4.844734000	-2.626669000	-3.789626000
H	5.410612000	-3.978721000	-2.772827000
H	3.731465000	-3.405421000	-2.628048000
C	5.522930000	-1.688407000	0.800844000
O	6.688567000	-1.631140000	1.203435000
N	4.524363000	-0.865023000	1.248874000
H	3.577475000	-1.000350000	0.909030000
C	4.721955000	0.088677000	2.312268000
H	5.678927000	-0.170221000	2.788223000
C	4.807054000	1.578410000	1.806687000
H	3.800252000	1.994926000	1.681034000
H	5.297943000	2.171932000	2.593952000
C	5.549768000	1.699058000	0.497503000
C	6.950041000	1.797537000	0.447816000
H	7.521353000	1.823137000	1.377683000
C	7.629845000	1.851125000	-0.777518000
H	8.720174000	1.925370000	-0.801996000
C	6.904808000	1.789050000	-1.981888000
O	7.511810000	1.811441000	-3.216645000
H	8.471799000	1.838875000	-3.082497000
C	5.502536000	1.686927000	-1.950558000
H	4.950209000	1.621168000	-2.887126000
C	4.840683000	1.642258000	-0.719507000
H	3.754852000	1.550726000	-0.709091000
C	3.563966000	-0.038580000	3.321146000
O	2.468318000	-0.541170000	3.030968000
N	3.810210000	0.508797000	4.543316000
H	4.719580000	0.873856000	4.791010000
H	3.077051000	0.499992000	5.241443000
Ni	0.168515000	0.876445000	-0.773852000

Table S5. Calculated vertical transitions for the $[NiL]^{2-}$ species formed in the Ni(II)/**wtPen** system on the WT conformation. The most important transitions are highlighted (in bold). [a]

Transition (% weight)	Main character [b]	λ^{calcd} [c]	f (×10^5) [d]
I (44.0)	Ni-d_{xy} → Ni-$d_{x^2-y^2}$ (LUMO)	502	120
II (56.5)	Ni-$d_{z^2/xz}$ → Ni-$d_{x^2-y^2}$ (LUMO)	332	220
III (91.5)	Ni-d_{yz} → L_{Pro5}	303	2150
IV (45.4)	Ni-$d_{z^2/xz}$ → Ni-$d_{x^2-y^2}$ (LUMO)	299	110
V (88.9)	Ni-d_{xz} → L_{Tyr8}	293	140
VI (82.6)	Ni-d_{yz} → L_{Tyr8}	286	110
VII (74.6)	Ni-d_{xz} → L_{Cys6}	279	220
VIII (70.7)	$L_{His1/Cys6}$ → Ni-$d_{x^2-y^2}$ (LUMO)	276	5580

IX (84.8)	Ni-d_{yz} → L_{Cys6}	275	150
X (33.8) X (57.7)	L_{Asp3} → Ni-$d_{x^2-y^2}$ Ni-d_{xz} → L_{Cys6}	268	590
XI (56.7) XII (28.4)	L_{Asp3} → Ni-$d_{x^2-y^2}$ Ni-d_{xz} → L_{Cys6}	267	860
XIII (65.5)	Ni-d_{yz} → L_{His1}	264	690
XIV (88.7)	Ni-d_{xz} → L_{Ala7}	263	460
XV (90.9)	Ni-d_{z^2} → L_{Tyr8}	262	350
XVI (18.0)	$L_{His1/Cys6}$ → Ni-$d_{x^2-y^2}$ (LUMO)	262	5240

[a] Transitions calculated with HSE06 functional and *def2*-TZVP basis-set. [b] The character of the orbital was assigned considering the largest contribution of the atomic orbitals to the specific MO. [c] λ values measured in nm. [d] Strength of the oscillator associated with the transition.

Table S6. Calculated vertical transitions for the $[NiL]^{2-}$ species formed in the Ni(II)/**wtSOD**. The most important transitions are given in bold. [a]

Transition (% weight)	Main character [b]	λ^{calcd} [c]	$f(\times 10^5)$ [d]
I (28.8)	**Ni-d_{xy} → Ni-$d_{x^2-y^2}$ (LUMO)**	**509**	**130**
II (26.4) **II (29.0)**	**Ni-d_{z^2} → Ni-$d_{x^2-y^2}$ (LUMO)** **Ni-d_{xz} → Ni-$d_{x^2-y^2}$ (LUMO)**	**335**	**200**
III (94.0)	**Ni-d_{xz} → L_{Pro5}**	**311**	**570**
IV (92.4)	**Ni-d_{yz} → L_{Pro5}**	**303**	**2280**
V (48.6)	Ni-$d_{z^2/xz}$ → Ni-$d_{x^2-y^2}$ (LUMO)	300	150
VI (91.3)	Ni-d_{xz} → L_{Tyr8}	292	150
VII (43.9)	Ni-d_{yz} → L_{Tyr8}	284	230
VIII (83.3)	Ni-d_{xz} → L_{Cys6}	279	180
IX (80.5)	Ni-d_{yz} → L_{Leu4}	277	670
X (51.7)	**$L_{His1/Cys6}$ → Ni-$d_{x^2-y^2}$ (LUMO)**	**277**	**4020**
XI (85.3)	Ni-d_{yz} → L_{Cys6}	275	100
XII (94.1)	**Ni-d_{z^2} → L_{Pro5}**	**273**	**140**
XIII (86.6)	**$L_{His1/Cys6}$ → Ni-$d_{x^2-y^2}$ (LUMO)**	**269**	**380**
XIV (67.4)	Ni-d_{xz} → L_{His1}	268	440
XVI (35.5)	**$L_{His1/Cys6}$ → Ni-$d_{x^2-y^2}$ (LUMO)**	**264**	**4380**

[a] Transitions calculated with HSE06 functional and *def2*-TZVP basis-set. [b] The character of the orbital was assigned considering the largest contribution of the atomic orbitals to the specific MO. [c] λ values measured in nm. [d] Strength of the oscillator associated with the transition.

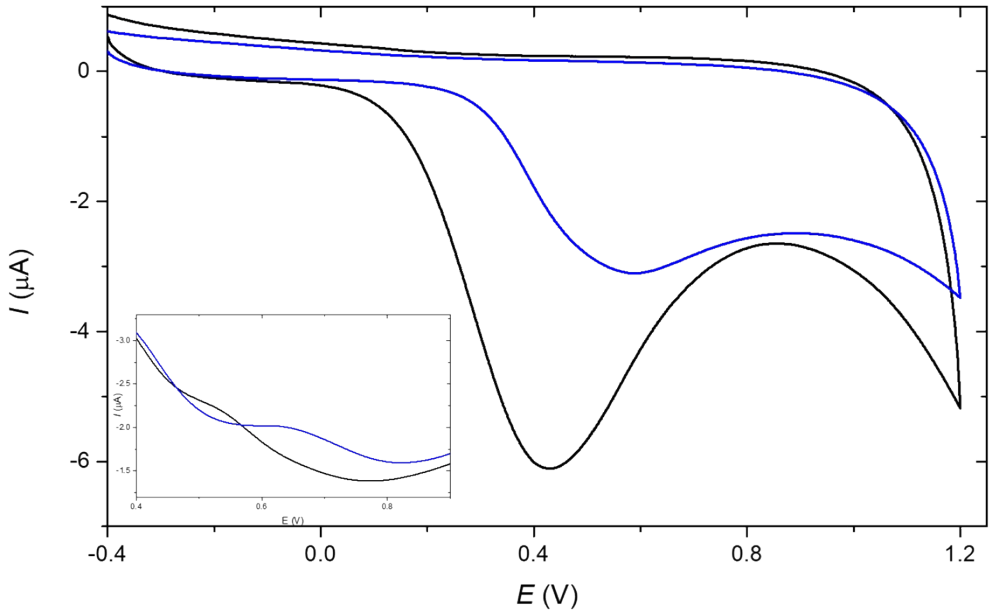


Figure S10. CV and DPC (inset) curves recorded in the Ni/**wtPen** (blue) and Ni/**wtSOD** (black) systems at pH 7.6 in 0.1 M $NaClO_4$. $c_{complex}$ = 2 mM

Nickel(III) complexes.

Table S7. Anisotropic EPR parameters of the oxidized form of nickel **wtPen** and **wtSOD** complexes. [a]

Complexes	g_x	g_y	g_z	$a^{N}{}_x$ [b]	$a^{N}{}_y$ [b]	$a^{N}{}_z$ [b]	w_x [b,c]	w_y [b,c]	w_z [b,c]
wtPen, pH 7.5	2.257	2.251	2.013	17.4	17.4	22.1	19.8	22.4	4.9
wtPen, pH 9.6	2.247	2.241	2.014	16.8	16.7	22.8	18.9	35.7	5.2
wtSOD[d]	2.289	2.220	2.012	18.7	18.2	23.7			

[a] Isotropic signal was taken into account to describe the background with parameters g_{iso} = 2.085 and w = 250 G. [b] Value in $10^{-4}\cdot cm^{-1}$ [c] Linewidth on the x, y, z axes. [d] Data are taken from ref. [31].

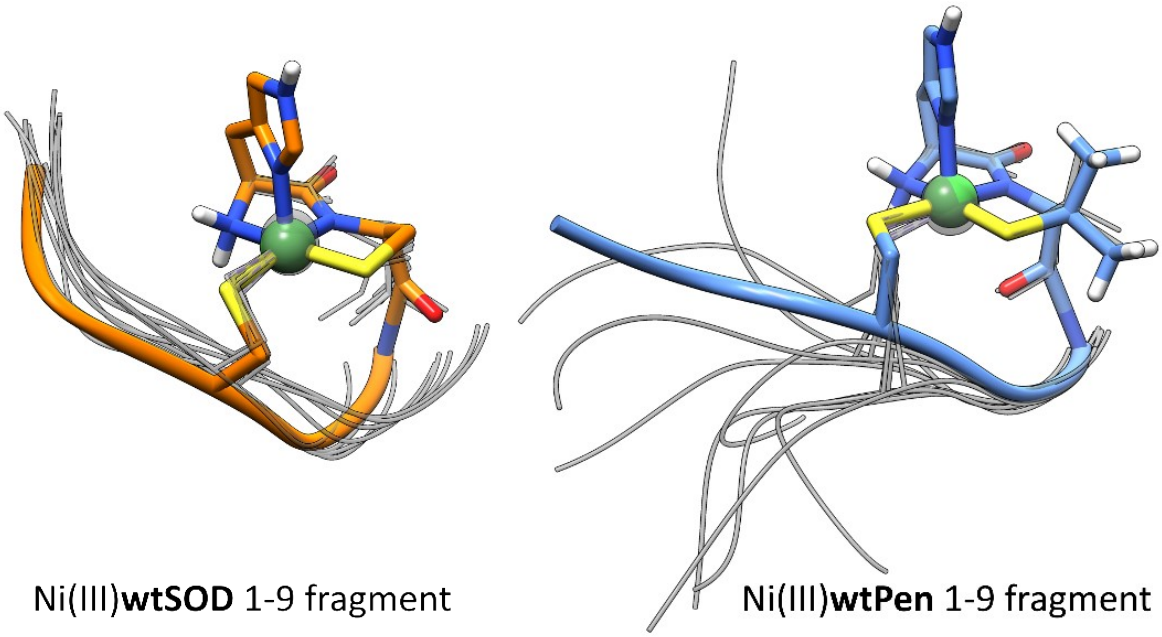


Figure S11. Representative structures for the most populated cluster obtained along the 200 ns MD for Ni(III)–**wtSOD** and Ni(III)–**wtPen** together with the most representative frames of the other identified clusters.

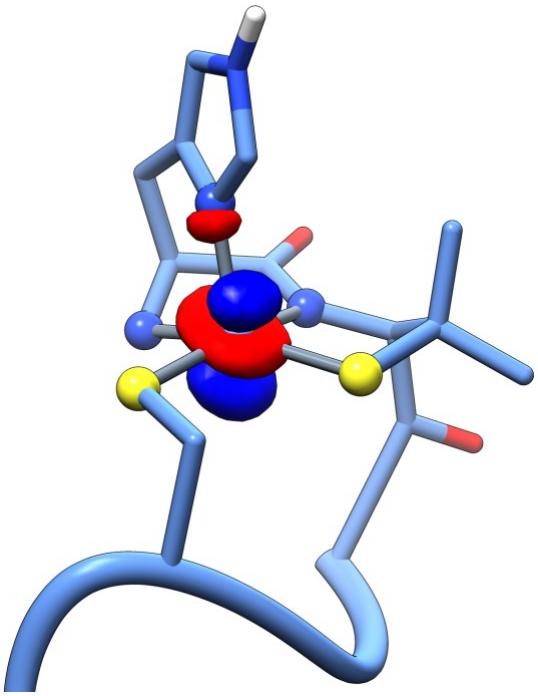


Figure S12. The MO HOMO-4 based on Ni-d_{z^2} orbital.

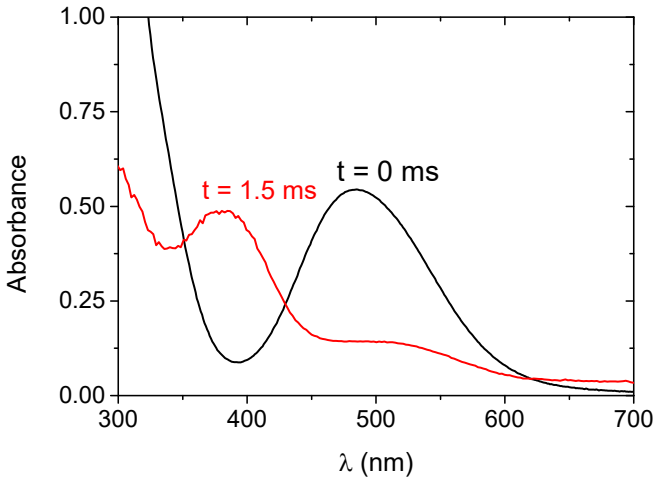


Figure S13. Electronic absorption spectra recorded in the Ni(II)/**wtPen** system in 1:1 aqueous HEPES buffer (50 mM, pH 7.6) / DMSO mixture before (black) and after mixing with KO_2. c(complex)^0 = 0.2 mM; $c(O_2^-)^0$ = 0.41 mM, l = 10 mm

Table S8. Comparison of the experimental values of selected spin Hamiltonian EPR parameters computed at B3LYP, BP and PBE0 DFT theory level for the $[Ni^{III}(mnt)_2]^-$, $[Ni^{III}(salophCl_2)]^+$, $[Ni^{III}(salophCl_2)(py)]^+$ and $[Ni^{III}(salophCl_2)(py)_2]^+$ benchmark dataset. [a,b]

Species		A_z [b,c]	g_x [d]	g_y [d]	g_z [d]
$[Ni^{III}(mnt)_2]^-$	Exptl.	15.0	2.160	2.042	1.998
	Calcd. (B3LYP)	11.5 (-23.3) [e]	2.144	2.079	2.014
	Calcd. (BP)	16.5 (10.1) [e]	2.113	2.038	2.000
	Calcd. (PBE0)	10.6 (-29.1) [e]	2.167	2.102	2.021
$[Ni^{III}(salophCl_2)]^+$	Exptl.	21.4	2.189	2.162	2.022
	Calcd. (B3LYP)	1.5 (-93.0) [f]	2.061 (-5.8)	2.026 (-6.3)	2.001 (-1.0)
	Calcd. (BP)	0.8 (-96.3) [f]	2.117 (-3.3)	2.021 (-6.5)	2.006 (-0.8)
	Calcd. (PBE0)	1.7 (-92.1) [f]	2.054 (-6.2)	2.028 (-6.2)	1.999 (-1.1)
$[Ni^{III}(salophCl_2)(py)]^+$	Exptl.	21.4	2.189	2.162	2.022
	Calcd. (B3LYP)	27.8 (29.9) [f]	2.176 (-0.6)	2.167 (0.2)	2.029 (0.3)
	Calcd. (BP)	26.2 (22.4) [f]	2.124 (-3.0)	2.109 (-2.5)	2.011 (-0.5)
	Calcd. (PBE0)	26.2 (22.4) [f]	2.202 (0.6)	2.193 (1.4)	2.043 (1.0)
$[Ni^{III}(salophCl_2)(py)_2]^+$	Exptl.	21.4	2.189	2.162	2.022
	Calcd. (B3LYP)	20.2 (-5.6) [f]	2.155 (-1.6)	2.144 (-0.8)	2.051 (1.4)
	Calcd. (BP)	21.9 (2.3) [f]	2.112 (-3.5)	2.095 (-3.1)	2.022 (0.0)
	Calcd. (PBE0)	18.8 (-12.1) [f]	2.177 (-0.5)	2.166 (0.2)	2.077 (2.7)

[a] Calculations carried out at BP/6-311g(d,p) theory level with ORCA 4.0 (see Supporting Information for selection of the method). [b] Value in $10^{-4}\cdot cm^{-1}$. [c] Percent deviation in parenthesis, calculated as $[(A^N{}_z{}^{calcd} - A^N{}_z{}^{exptl}) / A^N{}_z{}^{exptl}] \times 100$. [d] Percent deviation in parenthesis, calculated as $[(g_i^{calcd} - g_i^{exptl}) / g_i^{exptl}] \times 100$, with $i = x, y, z$. [e] A_z for ^{61}Ni nucleus. [f] $A^N{}_z$ for the axial py-N donors.

Table S9. Cartesian coordinates of $[Ni^{III}(mnt)_2]^-$.

Ni	0.000002000	0.000009000	0.000020000
S	1.540834000	-1.578836000	0.000180000
S	1.540840000	1.578844000	-0.000207000
S	-1.540837000	-1.578838000	-0.000066000
S	-1.540843000	1.578846000	0.000121000
N	5.235712000	-2.105226000	0.000114000
N	5.235738000	2.105191000	-0.000289000
N	-5.235707000	-2.105233000	-0.000239000
N	-5.235734000	2.105196000	0.000396000
C	3.047004000	-0.697833000	0.000035000
C	3.047005000	0.697834000	-0.000136000
C	4.253408000	-1.457389000	0.000131000
C	4.253412000	1.457387000	-0.000299000
C	-3.047004000	-0.697834000	-0.000007000
C	-3.047006000	0.697836000	0.000068000

C	-4.253409000	-1.457387000	-0.000083000
C	-4.253413000	1.457386000	0.000142000

Table S10. Cartesian coordinates of $[Ni^{III}(salophCl_2)]^+$.

Ni	0.000020000	0.414975000	-0.117248000
O	-1.244851000	-0.971385000	-0.155940000
O	1.244902000	-0.971400000	-0.155560000
N	-1.286887000	1.776331000	-0.030781000
N	1.286845000	1.776410000	-0.030345000
C	-2.586292000	1.596367000	0.072878000
C	2.586275000	1.596421000	0.073121000
C	-2.535452000	-0.906027000	-0.054270000
C	-3.309234000	-2.122635000	-0.063661000
C	-4.693881000	-2.107448000	0.053345000
C	-5.367035000	-0.869197000	0.183182000
C	-4.671235000	0.338243000	0.193052000
C	-3.261463000	0.336450000	0.074129000
C	2.535508000	-0.905990000	-0.054068000
C	3.309344000	-2.122565000	-0.063580000
C	4.694002000	-2.107321000	0.053267000
C	5.367115000	-0.869042000	0.183050000
C	4.671261000	0.338367000	0.193013000
C	3.261474000	0.336519000	0.074262000
H	-3.226684000	2.474064000	0.166737000
H	3.226740000	2.474059000	0.166895000
H	-5.253690000	-3.039950000	0.047403000
H	-5.202418000	1.283185000	0.289925000
H	5.253851000	-3.039799000	0.047240000
H	5.202415000	1.283331000	0.289843000
C	0.706183000	3.079510000	-0.058498000
C	-0.706328000	3.079431000	-0.058982000
C	1.413224000	4.294535000	-0.102801000
C	-1.413586000	4.294281000	-0.104110000
C	0.702267000	5.501729000	-0.139603000
C	-0.702838000	5.501609000	-0.140316000
H	2.499699000	4.320344000	-0.123635000
H	-2.500055000	4.319775000	-0.126023000
H	1.250711000	6.441754000	-0.179177000
H	-1.251414000	6.441529000	-0.180506000
Cl	-2.475245000	-3.647830000	-0.217526000
Cl	-7.109536000	-0.870068000	0.333025000
Cl	2.475401000	-3.647792000	-0.217378000
Cl	7.109633000	-0.869834000	0.332683000

Table S11. Cartesian coordinates of $[Ni^{III}(salophCl_2)(py)]^+$.

Ni	0.004051000	0.485660000	-0.701247000
O	-1.280855000	-0.831729000	-1.144161000
O	1.283118000	-0.844248000	-1.110486000
N	-1.292294000	1.878744000	-0.552096000
N	1.302465000	1.875277000	-0.540926000
C	-2.573228000	1.666499000	-0.351386000
C	2.583594000	1.660494000	-0.343357000

C	-2.518435000	-0.812655000	-0.731450000
C	-3.269777000	-2.033629000	-0.694100000
C	-4.605614000	-2.068364000	-0.305372000
C	-5.253002000	-0.869664000	0.071530000
C	-4.579595000	0.343323000	0.057219000
C	-3.214290000	0.388148000	-0.335169000
C	2.523500000	-0.821498000	-0.707034000
C	3.275597000	-2.042195000	-0.669957000
C	4.613794000	-2.075233000	-0.289905000
C	5.264052000	-0.874740000	0.076604000
C	4.590861000	0.338041000	0.060201000
C	3.222495000	0.381360000	-0.322746000
H	-3.217783000	2.528879000	-0.169599000
H	3.231724000	2.521983000	-0.170723000
H	-5.141503000	-3.014943000	-0.284178000
H	-5.081118000	1.263294000	0.352255000
H	5.149709000	-3.021792000	-0.268116000
H	5.094657000	1.259645000	0.346101000
C	0.715338000	3.166768000	-0.542809000
C	-0.702414000	3.168409000	-0.554225000
C	1.422348000	4.385207000	-0.517672000
C	-1.408376000	4.387644000	-0.548054000
C	0.711964000	5.589371000	-0.503572000
C	-0.696863000	5.590777000	-0.519765000
H	2.509492000	4.403964000	-0.530606000
H	-2.495025000	4.406486000	-0.585585000
H	1.258968000	6.531240000	-0.498759000
H	-1.242072000	6.533650000	-0.527931000
Cl	-2.474347000	-3.525741000	-1.157744000
Cl	-6.937832000	-0.937528000	0.570865000
Cl	2.477550000	-3.536503000	-1.122343000
Cl	6.952432000	-0.940568000	0.564594000
N	-0.017719000	0.003991000	1.339475000
C	-0.037882000	-1.299806000	1.694611000
C	-0.007925000	0.965397000	2.286455000
C	-0.048792000	-1.689906000	3.037651000
C	-0.017651000	0.650604000	3.649403000
C	-0.038180000	-0.699372000	4.031211000
H	-0.045339000	-2.016908000	0.877601000
H	0.007897000	1.995530000	1.935413000
H	-0.065019000	-2.749013000	3.288512000
H	-0.009131000	1.451870000	4.385965000
H	-0.045931000	-0.974702000	5.085391000

Table S12. Cartesian coordinates of $[Ni^{III}(salophCl_2)(py)_2]^+$.

Ni	0.000005000	0.317846000	-0.000169000
O	1.220531000	-1.083346000	0.488702000
O	-1.220593000	-1.082980000	-0.489966000
N	1.256340000	1.742038000	0.357241000
N	-1.256342000	1.742252000	-0.356682000
C	2.546630000	1.555630000	0.506906000
C	-2.546676000	1.555963000	-0.506124000
C	2.514869000	-0.965415000	0.484358000
C	3.327468000	-2.149433000	0.436275000

C	4.715928000	-2.105331000	0.498122000
C	5.367327000	-0.853479000	0.581385000
C	4.643318000	0.328242000	0.598309000
C	3.221176000	0.293970000	0.545331000
C	-2.514934000	-0.965082000	-0.484952000
C	-3.327509000	-2.149122000	-0.437129000
C	-4.715998000	-2.104984000	-0.498373000
C	-5.367427000	-0.853089000	-0.580710000
C	-4.643422000	0.328645000	-0.597321000
C	-3.221266000	0.294335000	-0.544952000
H	3.189081000	2.438025000	0.558859000
H	-3.189112000	2.438403000	-0.557499000
H	5.292433000	-3.027779000	0.474141000
H	5.151745000	1.289925000	0.643196000
H	-5.292491000	-3.027445000	-0.474623000
H	-5.151866000	1.290353000	-0.641477000
C	-0.664017000	3.019481000	-0.253354000
C	0.664095000	3.019342000	0.254385000
C	-1.294369000	4.239611000	-0.573182000
C	1.294515000	4.239316000	0.574668000
C	-0.640647000	5.442432000	-0.293873000
C	0.640860000	5.442279000	0.295808000
H	-2.284583000	4.251768000	-1.023053000
H	2.284741000	4.251265000	1.024520000
H	-1.134928000	6.385342000	-0.524251000
H	1.135214000	6.385070000	0.526519000
Cl	2.526061000	-3.708322000	0.327955000
Cl	7.127039000	-0.814520000	0.646063000
Cl	-2.526068000	-3.708066000	-0.329940000
Cl	-7.127164000	-0.814088000	-0.644613000
N	0.776049000	0.234323000	-2.052136000
C	1.061259000	-0.982874000	-2.562188000
C	1.005475000	1.332923000	-2.800240000
C	1.591191000	-1.145670000	-3.847354000
C	1.530531000	1.257203000	-4.095751000
C	1.830387000	-0.005325000	-4.628945000
H	0.860397000	-1.828683000	-1.908221000
H	0.762811000	2.291438000	-2.345456000
H	1.810593000	-2.145743000	-4.217991000
H	1.698584000	2.170341000	-4.664458000
H	2.243039000	-0.098384000	-5.633316000
N	-0.775997000	0.233093000	2.051731000
C	-1.005436000	1.331273000	2.800448000
C	-1.061178000	-0.984394000	2.561103000
C	-1.530473000	1.254820000	4.095922000
C	-1.591097000	-1.147917000	3.846182000
C	-1.830303000	-0.008012000	4.628411000
H	-0.762801000	2.290045000	2.346187000
H	-0.860297000	-1.829831000	1.906662000
H	-1.698535000	2.167636000	4.665143000
H	-1.810482000	-2.148201000	4.216262000
H	-2.242943000	-0.101640000	5.632735000

Table S13. Cartesian coordinates of the extended conformation of Ni^{III}/**wtSOD** complex.

N	0.746871000	0.061837000	0.041883000
C	0.925257000	1.249971000	0.926045000
C	-0.318037000	2.148093000	0.796263000
O	-0.635662000	2.942471000	1.712881000
C	2.206821000	2.021158000	0.541204000
C	2.273277000	2.553001000	-0.867960000
N	1.580184000	1.980821000	-1.922677000
C	3.055598000	3.582541000	-1.356833000
C	1.920057000	2.638035000	-3.023620000
N	2.820254000	3.616909000	-2.722533000
H	1.033707000	0.941361000	1.976295000
H	2.302009000	2.857297000	1.244935000
H	3.061488000	1.355834000	0.725860000
H	3.767855000	4.246627000	-0.882446000
H	1.520112000	2.449363000	-4.012551000
H	0.079635000	-0.583831000	0.465780000
H	1.637808000	-0.441977000	-0.040126000
H	3.228939000	4.270791000	-3.377905000
N	-0.935698000	1.990437000	-0.389954000
C	-2.049323000	2.888505000	-0.750979000
C	-3.392588000	2.363185000	-0.180273000
O	-4.314435000	1.953092000	-0.916926000
C	-2.071390000	3.033226000	-2.271901000
S	-1.639226000	1.435528000	-3.111924000
H	-1.868306000	3.871826000	-0.280724000
H	-3.064349000	3.344135000	-2.624197000
H	-1.323546000	3.781915000	-2.570263000
N	-3.444288000	2.384813000	1.174262000
H	-2.637616000	2.813118000	1.636796000
C	-4.649665000	2.211324000	2.008597000
H	-4.333221000	2.477266000	3.022478000
C	-5.768542000	3.198814000	1.614200000
H	-6.661176000	2.961164000	2.216417000
H	-6.036130000	3.072846000	0.557289000
C	-5.366152000	4.680327000	1.893516000
O	-6.036879000	5.563209000	1.279634000
O	-4.434241000	4.908426000	2.717984000
C	-5.192307000	0.768594000	2.102673000
O	-5.637897000	0.330647000	3.169884000
N	-5.168019000	0.052854000	0.938780000
H	-4.953159000	0.577174000	0.082108000
C	-5.700551000	-1.301488000	0.844109000
H	-6.782140000	-1.295012000	1.047191000
C	-5.457346000	-1.863161000	-0.572290000
H	-4.377705000	-1.888109000	-0.773983000
H	-5.813528000	-2.905708000	-0.582829000
C	-6.137796000	-1.083783000	-1.721026000
H	-5.739595000	-0.057220000	-1.738682000

C	-5.767399000	-1.746528000	-3.061289000
H	-4.674870000	-1.765650000	-3.200978000
H	-6.211490000	-1.199926000	-3.907235000
H	-6.135813000	-2.785422000	-3.094192000
C	-7.664286000	-1.011707000	-1.543710000
H	-7.938378000	-0.464155000	-0.630011000
H	-8.130052000	-0.498583000	-2.398973000
H	-8.093539000	-2.025358000	-1.478290000
C	-5.159661000	-2.265251000	1.931794000
O	-5.936957000	-3.031357000	2.510864000
N	-3.821955000	-2.244130000	2.242760000
C	-3.344062000	-3.091130000	3.354530000
H	-3.650080000	-4.133439000	3.195934000
H	-3.806873000	-2.735111000	4.287413000
C	-1.809202000	-2.917349000	3.341625000
H	-1.387582000	-2.845389000	4.352862000
H	-1.346963000	-3.769221000	2.826304000
C	-1.581359000	-1.633185000	2.514924000
H	-0.572522000	-1.595481000	2.077833000
H	-1.729154000	-0.729430000	3.123289000
C	-2.714973000	-1.699454000	1.458196000
H	-2.963614000	-0.709121000	1.058212000
C	-2.330937000	-2.674827000	0.318379000
O	-2.496240000	-3.892810000	0.398654000
N	-1.718901000	-2.086230000	-0.768505000
C	-1.450126000	-2.881210000	-1.972781000
C	-0.342244000	-3.944732000	-1.818826000
O	-0.225307000	-4.833447000	-2.665004000
C	-1.100849000	-1.978844000	-3.176405000
S	0.439708000	-0.973201000	-3.005336000
H	-1.789098000	-1.075744000	-0.893834000
H	-2.356927000	-3.454724000	-2.224944000
H	-1.947990000	-1.310664000	-3.386439000
H	-0.960973000	-2.648470000	-4.035803000
N	0.511579000	-3.781556000	-0.762897000
H	0.333847000	-3.013690000	-0.128719000
C	1.700060000	-4.588154000	-0.574838000
H	1.673528000	-5.140044000	0.376642000
H	1.723106000	-5.322722000	-1.393667000
C	3.008589000	-3.781983000	-0.572001000
O	4.007130000	-4.223398000	0.023391000
N	3.007895000	-2.599740000	-1.238816000
H	2.155445000	-2.255299000	-1.698813000
C	4.165195000	-1.711905000	-1.144867000
H	5.053363000	-2.255954000	-1.509502000
C	3.950026000	-0.455235000	-2.025354000
H	2.958679000	-0.048910000	-1.782811000
C	4.997373000	0.631815000	-1.736440000
H	4.949089000	0.996885000	-0.703891000
H	6.016300000	0.251716000	-1.915582000

H	4.830136000	1.486175000	-2.406247000
C	3.970213000	-0.843203000	-3.514505000
H	3.723874000	0.033599000	-4.130229000
H	4.974388000	-1.197228000	-3.799795000
H	3.239096000	-1.630011000	-3.740171000
C	4.368558000	-1.343931000	0.348851000
O	3.415980000	-0.982579000	1.056487000
N	5.654664000	-1.435067000	0.783992000
H	6.312707000	-1.857526000	0.141357000
C	6.131378000	-1.250526000	2.160263000
H	7.226828000	-1.186013000	2.079147000
C	5.628907000	0.043372000	2.840170000
H	4.557211000	-0.064876000	3.046443000
H	6.143579000	0.074745000	3.812242000
C	5.853481000	1.323715000	2.059280000
C	6.891575000	1.494559000	1.125500000
H	7.587854000	0.679616000	0.927256000
C	7.036150000	2.688871000	0.403532000
H	7.832300000	2.789625000	-0.337675000
C	6.134248000	3.746614000	0.613425000
O	6.173719000	4.922436000	-0.100385000
H	6.918058000	4.884732000	-0.721243000
C	5.114937000	3.612854000	1.572547000
H	4.428344000	4.442744000	1.739727000
C	4.983606000	2.411179000	2.274698000
H	4.171361000	2.302965000	2.995532000
C	5.876245000	-2.459974000	3.111820000
O	6.237338000	-2.382002000	4.289685000
N	5.302428000	-3.560887000	2.563934000
H	4.941903000	-3.620083000	1.611242000
H	5.127495000	-4.337591000	3.188868000
Ni	-0.165906000	0.751995000	-1.662743000

Table S14. Cartesian coordinates of the α-helix conformation of Ni^{III}/**wtSOD** complex.

N	4.675257000	-0.907759000	1.565364000
C	6.057490000	-0.356251000	1.576270000
C	6.112101000	0.818867000	0.571912000
O	6.991415000	1.690358000	0.623890000
C	7.094604000	-1.440392000	1.218860000
C	6.945424000	-2.013410000	-0.170554000
N	5.746905000	-2.002160000	-0.867544000
C	7.895137000	-2.639369000	-0.953461000
C	5.952640000	-2.596692000	-2.036093000
N	7.248655000	-3.001884000	-2.123843000
H	6.278026000	0.062830000	2.568506000
H	8.093933000	-0.993640000	1.317468000
H	7.029429000	-2.249460000	1.968433000
H	8.942532000	-2.855847000	-0.783129000
H	5.208783000	-2.722270000	-2.812627000

H	4.060972000	-0.245944000	2.130632000
H	4.642706000	-1.843043000	1.976991000
H	7.667114000	-3.480037000	-2.911324000
N	5.115241000	0.733946000	-0.348647000
C	4.849959000	1.842446000	-1.262908000
C	3.805394000	2.837844000	-0.676791000
O	3.724944000	4.002405000	-1.075830000
C	4.372434000	1.238003000	-2.589976000
S	3.176150000	-0.150879000	-2.268117000
H	5.763766000	2.434199000	-1.421065000
H	3.877846000	1.991235000	-3.221134000
H	5.235396000	0.825708000	-3.132572000
N	2.962438000	2.265364000	0.239752000
H	3.279786000	1.370883000	0.605421000
C	2.199531000	2.988243000	1.258821000
H	1.598037000	2.199069000	1.728064000
C	3.116146000	3.422352000	2.406379000
H	2.513789000	3.917860000	3.183832000
H	3.888887000	4.125717000	2.068037000
C	3.825258000	2.135219000	2.998867000
O	4.917112000	2.281998000	3.575618000
O	3.200265000	1.012273000	2.795657000
C	1.083548000	3.886864000	0.705877000
O	0.472096000	4.687323000	1.417552000
N	0.667330000	3.509371000	-0.555233000
H	1.272380000	2.848442000	-1.031111000
C	-0.721527000	3.546718000	-1.018382000
H	-1.001956000	4.572654000	-1.289699000
C	-0.823645000	2.636657000	-2.266119000
H	-0.143468000	3.050401000	-3.030976000
H	-0.436833000	1.636729000	-2.009662000
C	-2.233511000	2.488823000	-2.868404000
H	-2.880891000	2.030269000	-2.109075000
C	-2.849806000	3.848382000	-3.240936000
H	-2.197345000	4.391223000	-3.945846000
H	-2.999938000	4.465514000	-2.344665000
H	-3.827681000	3.701480000	-3.724294000
C	-2.179307000	1.538793000	-4.078317000
H	-1.493784000	1.932245000	-4.847608000
H	-1.840858000	0.533576000	-3.785551000
H	-3.176861000	1.437342000	-4.531433000
C	-1.759380000	3.173743000	0.074871000
O	-2.745290000	3.902663000	0.241173000
N	-1.568210000	2.045326000	0.845609000
C	-2.224045000	1.946247000	2.164261000
H	-2.993129000	1.160439000	2.153365000
H	-2.691109000	2.906185000	2.406897000
C	-1.046636000	1.557009000	3.071098000
H	-0.419983000	2.443813000	3.245086000
H	-1.368290000	1.141590000	4.036187000

C	-0.290944000	0.525317000	2.211192000
H	-0.758639000	-0.462082000	2.345370000
H	0.779673000	0.450509000	2.448004000
C	-0.522127000	1.022022000	0.734081000
H	0.390891000	1.435299000	0.305431000
C	-0.941576000	-0.199161000	-0.090141000
O	-2.120920000	-0.585294000	-0.159624000
N	0.102830000	-0.902654000	-0.587618000
C	0.002321000	-2.280547000	-1.079376000
C	-0.679671000	-3.242769000	-0.077749000
O	-1.325835000	-4.219642000	-0.467952000
C	1.417978000	-2.825953000	-1.420619000
S	2.660704000	-2.654782000	-0.057796000
H	1.042953000	-0.516820000	-0.494302000
H	-0.626802000	-2.311107000	-1.980769000
H	1.791329000	-2.328126000	-2.325705000
H	1.306772000	-3.895298000	-1.647894000
N	-0.478621000	-2.965738000	1.247841000
H	0.240373000	-2.288773000	1.481757000
C	-1.044939000	-3.811805000	2.289386000
H	-0.907009000	-4.871631000	2.033791000
H	-0.515591000	-3.609946000	3.229772000
C	-2.565024000	-3.637197000	2.546019000
O	-3.145342000	-4.428218000	3.292708000
N	-3.149521000	-2.570273000	1.925764000
H	-2.591288000	-2.021730000	1.274169000
C	-4.600676000	-2.361598000	1.883015000
H	-5.053595000	-3.116880000	2.536569000
C	-4.984137000	-0.936697000	2.361908000
H	-4.475995000	-0.216243000	1.701543000
C	-6.498043000	-0.701090000	2.221681000
H	-6.759091000	0.305939000	2.577131000
H	-6.816857000	-0.778021000	1.173427000
H	-7.059731000	-1.436826000	2.819908000
C	-4.507623000	-0.700130000	3.804228000
H	-5.021200000	-1.386735000	4.495826000
H	-3.425509000	-0.870518000	3.896872000
H	-4.729007000	0.331803000	4.116315000
C	-5.082744000	-2.658407000	0.438742000
O	-5.774827000	-3.646977000	0.146383000
N	-4.652767000	-1.739422000	-0.462373000
H	-3.946305000	-1.067543000	-0.177911000
C	-4.876236000	-1.804429000	-1.904521000
H	-5.838433000	-2.315737000	-2.052798000
C	-4.889604000	-0.372331000	-2.490004000
H	-3.844872000	-0.050343000	-2.581381000
H	-5.298676000	-0.425219000	-3.509893000
C	-5.664075000	0.613491000	-1.639356000
C	-7.058317000	0.765993000	-1.760420000
H	-7.597711000	0.183826000	-2.511293000

C	-7.769632000	1.650688000	-0.938422000
H	-8.849145000	1.768706000	-1.034541000
C	-7.081048000	2.414432000	0.023247000
O	-7.820404000	3.278667000	0.797898000
H	-7.211537000	3.739472000	1.395919000
C	-5.687687000	2.279108000	0.158463000
H	-5.127252000	2.893274000	0.866140000
C	-4.999038000	1.375449000	-0.658987000
H	-3.925276000	1.256502000	-0.516340000
C	-3.721924000	-2.667432000	-2.503720000
O	-2.780908000	-2.184756000	-3.140541000
N	-3.833973000	-3.999501000	-2.205742000
H	-4.514933000	-4.254531000	-1.490186000
H	-2.948463000	-4.497409000	-2.171385000
Ni	4.066798000	-0.891550000	-0.374942000

Table S15. Cartesian coordinates of the extended conformation of Ni^{III}/**wtPen** complex.

N	1.354074000	2.217337000	-1.649315000
C	2.124179000	3.352862000	-2.226875000
C	3.505144000	3.345619000	-1.523084000
O	4.516589000	3.768399000	-2.102019000
C	1.375760000	4.694211000	-2.058104000
C	1.247476000	5.160822000	-0.634296000
N	1.005335000	4.270443000	0.394208000
C	1.324785000	6.437028000	-0.114527000
C	0.932776000	4.971246000	1.514670000
N	1.117060000	6.298243000	1.251353000
H	2.304940000	3.200450000	-3.301624000
H	1.929602000	5.447608000	-2.635372000
H	0.374895000	4.602014000	-2.520125000
H	1.504276000	7.401044000	-0.575295000
H	0.777546000	4.553698000	2.502205000
H	1.784914000	1.337436000	-1.947535000
H	0.362217000	2.223938000	-1.893482000
H	1.130477000	7.043527000	1.934584000
N	3.429741000	2.843766000	-0.263233000
C	4.630783000	2.258149000	0.309677000
C	4.914082000	0.907602000	-0.433542000
O	4.110682000	0.423080000	-1.254180000
C	4.420241000	2.179590000	1.845894000
S	2.719125000	1.405863000	2.116601000
H	5.504371000	2.903030000	0.111965000
C	5.463343000	1.355618000	2.620945000
C	4.394227000	3.620184000	2.401043000
H	5.266130000	1.442781000	3.700101000
H	6.477666000	1.727901000	2.411333000
H	5.437023000	0.295690000	2.342105000
H	4.154029000	3.612400000	3.474716000
H	5.388515000	4.077826000	2.264507000

H	3.649897000	4.222219000	1.863659000
N	6.113563000	0.373849000	-0.123304000
H	6.848878000	0.967046000	0.360214000
C	6.782020000	-0.659316000	-0.916321000
H	6.867626000	-0.334687000	-1.965429000
C	8.198085000	-0.889629000	-0.309608000
H	8.766914000	-1.533572000	-0.989456000
H	8.071318000	-1.429545000	0.644801000
C	9.022216000	0.411954000	0.029415000
O	8.399323000	1.365146000	0.610565000
O	10.243986000	0.365837000	-0.254331000
C	6.071666000	-2.028075000	-0.956838000
O	6.302278000	-2.836298000	-1.858536000
N	5.270961000	-2.305957000	0.119574000
H	5.099314000	-1.558531000	0.783226000
C	4.659162000	-3.614373000	0.356533000
H	5.452813000	-4.345925000	0.566949000
C	3.731144000	-3.495335000	1.587323000
H	4.367563000	-3.294402000	2.468138000
H	3.084485000	-2.613197000	1.463012000
C	2.850215000	-4.727730000	1.870363000
H	2.203921000	-4.886881000	0.994217000
C	3.697538000	-5.993676000	2.092511000
H	4.253255000	-6.250905000	1.180851000
H	3.052292000	-6.846219000	2.358202000
H	4.413337000	-5.839492000	2.918853000
C	1.943409000	-4.438724000	3.079031000
H	2.547575000	-4.259022000	3.984900000
H	1.321909000	-3.548409000	2.898526000
H	1.272975000	-5.288962000	3.277354000
C	3.954544000	-4.237333000	-0.882879000
O	4.202945000	-5.407232000	-1.199815000
N	3.056610000	-3.485234000	-1.584635000
C	2.461507000	-4.032197000	-2.817915000
H	1.937073000	-4.973317000	-2.603124000
H	3.272271000	-4.245828000	-3.531241000
C	1.506939000	-2.916708000	-3.307244000
H	1.523494000	-2.809709000	-4.401142000
H	0.481269000	-3.144439000	-2.987806000
C	2.001013000	-1.649173000	-2.574903000
H	1.217673000	-0.883467000	-2.467162000
H	2.877475000	-1.202064000	-3.063049000
C	2.463569000	-2.207539000	-1.207900000
H	3.199884000	-1.541642000	-0.751409000
C	1.237647000	-2.409901000	-0.294710000
O	0.551352000	-3.437290000	-0.298017000
N	0.923840000	-1.316835000	0.466029000
C	-0.257796000	-1.307030000	1.320497000
C	-1.550318000	-1.667479000	0.554838000
O	-2.343677000	-2.502244000	1.022884000

C	-0.411657000	0.070271000	2.025310000
S	-0.392568000	1.566186000	0.943347000
H	1.550102000	-0.512901000	0.493734000
H	-0.169573000	-2.084500000	2.095511000
H	0.377111000	0.164532000	2.784704000
H	-1.382877000	0.075761000	2.539178000
N	-1.740098000	-0.958857000	-0.595980000
H	-1.172032000	-0.103954000	-0.628618000
C	-3.046088000	-0.868397000	-1.213868000
H	-2.929128000	-0.546683000	-2.260034000
H	-3.513442000	-1.861218000	-1.223132000
C	-3.977379000	0.123779000	-0.466821000
O	-3.733353000	0.556617000	0.659545000
N	-5.075414000	0.485913000	-1.201736000
H	-5.322908000	-0.046715000	-2.031760000
C	-6.160210000	1.285877000	-0.642681000
H	-5.998195000	1.334903000	0.444517000
C	-6.162742000	2.740810000	-1.202507000
H	-6.374717000	2.669626000	-2.283420000
C	-7.261155000	3.586682000	-0.530219000
H	-7.249404000	4.612004000	-0.929216000
H	-8.264080000	3.164693000	-0.682240000
H	-7.077836000	3.649726000	0.555722000
C	-4.782787000	3.393003000	-0.998603000
H	-4.791153000	4.425088000	-1.382052000
H	-4.523079000	3.415318000	0.070132000
H	-3.997262000	2.830085000	-1.519624000
C	-7.475386000	0.544744000	-0.963611000
O	-7.625406000	-0.071992000	-2.024292000
N	-8.445658000	0.651495000	-0.005948000
H	-8.241106000	1.145317000	0.854731000
C	-9.602854000	-0.224796000	0.032109000
H	-9.720170000	-0.636411000	-0.978981000
C	-9.371356000	-1.401695000	1.048102000
H	-9.393948000	-0.965262000	2.059481000
H	-10.226245000	-2.091926000	0.963800000
C	-8.058501000	-2.104173000	0.800908000
C	-6.881798000	-1.657640000	1.432536000
H	-6.943890000	-0.857461000	2.174108000
C	-5.630069000	-2.205434000	1.130258000
H	-4.726619000	-1.833328000	1.609962000
C	-5.532359000	-3.234646000	0.166269000
O	-4.352217000	-3.796745000	-0.195361000
H	-3.601025000	-3.345698000	0.287522000
C	-6.707585000	-3.701494000	-0.465785000
H	-6.621181000	-4.499110000	-1.204023000
C	-7.946140000	-3.134547000	-0.152514000
H	-8.843997000	-3.490699000	-0.664618000
C	-10.830086000	0.587431000	0.477073000
O	-10.760363000	1.444127000	1.358418000

N	-12.008715000	0.213871000	-0.116410000
H	-12.018482000	-0.374944000	-0.937886000
H	-12.848627000	0.724253000	0.127038000
Ni	1.711056000	2.212435000	0.374369000

Table S16. Cartesian coordinates of the α-helix conformation of Ni^{III}/**wtPen** complex.

N	4.522272000	-1.120251000	1.723151000
C	5.908973000	-0.584611000	1.776351000
C	5.990494000	0.641624000	0.837514000
O	6.889730000	1.487736000	0.940636000
C	6.940229000	-1.656889000	1.370735000
C	6.788349000	-2.165245000	-0.043372000
N	5.590478000	-2.110871000	-0.739446000
C	7.728829000	-2.778161000	-0.847587000
C	5.786640000	-2.672210000	-1.926139000
N	7.076312000	-3.092959000	-2.028595000
H	6.123173000	-0.219224000	2.790884000
H	7.941809000	-1.220761000	1.491652000
H	6.869372000	-2.500618000	2.080489000
H	8.772058000	-3.018747000	-0.684226000
H	5.043017000	-2.756084000	-2.708068000
H	3.902780000	-0.489681000	2.318083000
H	4.477653000	-2.078513000	2.076409000
H	7.487603000	-3.550232000	-2.832116000
N	4.993411000	0.633607000	-0.086348000
C	4.753132000	1.806139000	-0.924756000
C	3.758251000	2.782410000	-0.237231000
O	3.782296000	3.997978000	-0.445194000
C	4.286143000	1.305383000	-2.317089000
S	3.057008000	-0.098928000	-2.038267000
H	5.681604000	2.384122000	-1.045652000
N	2.832345000	2.151211000	0.555075000
H	3.084917000	1.205330000	0.828849000
C	2.071300000	2.814547000	1.615365000
H	1.444352000	2.009616000	2.018981000
C	2.977010000	3.153366000	2.802044000
H	2.370192000	3.597087000	3.606855000
H	3.760636000	3.869775000	2.523439000
C	3.662694000	1.816103000	3.300879000
O	4.766514000	1.901391000	3.869266000
O	3.011836000	0.722362000	3.034492000
C	0.991354000	3.773144000	1.089978000
O	0.376249000	4.547361000	1.826134000
N	0.615250000	3.481187000	-0.207916000
H	1.214148000	2.807953000	-0.677056000
C	-0.755381000	3.568645000	-0.716771000
H	-1.009324000	4.613440000	-0.936907000
C	-0.823012000	2.734796000	-2.019025000

H	-0.108382000	3.180745000	-2.732636000
H	-0.460037000	1.715425000	-1.807820000
C	-2.210454000	2.645428000	-2.681428000
H	-2.894391000	2.158122000	-1.973875000
C	-2.789342000	4.034515000	-3.000966000
H	-2.102011000	4.602243000	-3.650998000
H	-2.961854000	4.604909000	-2.078119000
H	-3.751125000	3.932793000	-3.526389000
C	-2.124220000	1.762026000	-3.938961000
H	-1.402912000	2.184258000	-4.658665000
H	-1.812845000	0.736639000	-3.689176000
H	-3.104810000	1.703054000	-4.434640000
C	-1.840918000	3.151114000	0.312918000
O	-2.819892000	3.888041000	0.485204000
N	-1.698971000	1.976485000	1.023007000
C	-2.407020000	1.813334000	2.307912000
H	-3.188166000	1.044216000	2.222123000
H	-2.867019000	2.766210000	2.588812000
C	-1.272069000	1.350049000	3.234080000
H	-0.638691000	2.213541000	3.484019000
H	-1.637858000	0.885058000	4.160044000
C	-0.500027000	0.356422000	2.344139000
H	-0.986024000	-0.629371000	2.404798000
H	0.560179000	0.249655000	2.613867000
C	-0.669138000	0.939731000	0.890472000
H	0.266490000	1.356815000	0.519000000
C	-1.080931000	-0.224490000	-0.016373000
O	-2.264475000	-0.580217000	-0.149647000
N	-0.032440000	-0.920220000	-0.514762000
C	-0.137769000	-2.265678000	-1.088533000
C	-0.866173000	-3.270846000	-0.165459000
O	-1.514036000	-4.213365000	-0.630320000
C	1.279542000	-2.815301000	-1.417094000
S	2.486901000	-2.731455000	-0.015152000
H	0.910446000	-0.560918000	-0.361931000
H	-0.738146000	-2.233529000	-2.009185000
H	1.685750000	-2.277262000	-2.284311000
H	1.159164000	-3.869874000	-1.701775000
N	-0.706016000	-3.070462000	1.179462000
H	0.016138000	-2.421156000	1.474263000
C	-1.324130000	-3.960132000	2.152960000
H	-1.192157000	-5.007578000	1.847902000
H	-0.828673000	-3.815906000	3.121990000
C	-2.850396000	-3.773476000	2.360572000
O	-3.471161000	-4.593027000	3.041068000
N	-3.394350000	-2.665436000	1.776623000
H	-2.803180000	-2.091916000	1.177757000
C	-4.839322000	-2.429749000	1.690347000
H	-5.328674000	-3.211188000	2.284155000
C	-5.219273000	-1.026287000	2.231484000

H	-4.674371000	-0.280144000	1.631745000
C	-6.722748000	-0.757171000	2.046502000
H	-6.982107000	0.233580000	2.446233000
H	-7.001316000	-0.771922000	0.984168000
H	-7.318735000	-1.514260000	2.581590000
C	-4.796310000	-0.876600000	3.701852000
H	-5.346920000	-1.590845000	4.334437000
H	-3.721344000	-1.070249000	3.826532000
H	-5.014295000	0.140519000	4.061372000
C	-5.270175000	-2.640147000	0.215129000
O	-5.964921000	-3.600156000	-0.155800000
N	-4.794051000	-1.680950000	-0.618303000
H	-4.088214000	-1.037758000	-0.272477000
C	-4.965151000	-1.664616000	-2.069044000
H	-5.929544000	-2.149339000	-2.279437000
C	-4.932642000	-0.203395000	-2.576816000
H	-3.879802000	0.103110000	-2.613228000
H	-5.304511000	-0.194718000	-3.612182000
C	-5.721269000	0.751090000	-1.703675000
C	-7.106529000	0.939313000	-1.869188000
H	-7.627323000	0.409253000	-2.670115000
C	-7.832167000	1.794549000	-1.028709000
H	-8.904635000	1.940410000	-1.159349000
C	-7.167130000	2.492146000	-0.002374000
O	-7.919396000	3.330348000	0.788294000
H	-7.325622000	3.745853000	1.432874000
C	-5.782953000	2.320234000	0.178333000
H	-5.238537000	2.884512000	0.938192000
C	-5.080666000	1.446075000	-0.659383000
H	-4.015917000	1.296483000	-0.482449000
C	-3.803933000	-2.515552000	-2.672229000
O	-2.832027000	-2.016501000	-3.247089000
N	-3.949095000	-3.859431000	-2.451573000
H	-4.660376000	-4.139381000	-1.775814000
H	-3.073839000	-4.374764000	-2.411527000
Ni	3.931759000	-0.978232000	-0.217092000
C	5.513762000	0.746049000	-3.063155000
H	6.028221000	0.002701000	-2.440961000
H	5.212576000	0.279564000	-4.012219000
H	6.214679000	1.569465000	-3.280983000
C	3.600510000	2.391765000	-3.162920000
H	4.294409000	3.233274000	-3.309532000
H	3.324343000	1.983914000	-4.146471000
H	2.698638000	2.783291000	-2.674681000

Table S17. Calculated vertical transitions for the $[NiL]^{2-}$ species formed in the Ni(III)/**wtPen** system. The most important transitions are given in bold. [a]

Transition (% weight)	**Main character** [b]	**λ^{calcd}** [c]	**f ($\times 10^5$)** [d]
I (55.8)	$L_{Asp3} \rightarrow$ Ni-$d_{x^2-y^2}$ (L+1)	342	64
II (24.7)	**$L_{Cys6} \rightarrow$ Ni-$d_{x^2-y^2}$ (L+1)**	**337**	**127**
III (75.1)	$L_{Cys6} \rightarrow$ Ni-$d_{x^2-y^2}$ (LUMO)	336	29
IV (69.0)	**$L_{His1} \rightarrow$ Ni-$d_{x^2-y^2}$ (L+1)**	**329**	**273**
IV (42.1)	**$L_{Asp3} \rightarrow$ Ni-$d_{x^2-y^2}$ (L+1)**		
V (33.7)	**$L_{Tyr9} \rightarrow$ Ni-$d_{x^2-y^2}$ (LUMO)**		
V (46.5)	**$L_{Asp3} \rightarrow$ Ni-$d_{x^2-y^2}$ (LUMO)**	**328**	**166**
V (25.0)	**$L_{Cys6} \rightarrow$ Ni-$d_{x^2-y^2}$ (L+1)**		
VI (24.6)	$L_{Asp3} \rightarrow$ Ni-$d_{x^2-y^2}$ (LUMO)	327	68
VI (86.2)	$L_{Asp3} \rightarrow$ Ni-$d_{x^2-y^2}$ (LUMO)		

[a] Transitions calculated with HSE06 functional and *def2*-TZVP basis-set. [b] The character of the orbital was assigned considering the largest contribution of the atomic orbitals to the specific MO. [c] λ values measured in nm. [d] Strength of the oscillator associated with the transition.

Stability of the metallopeptides

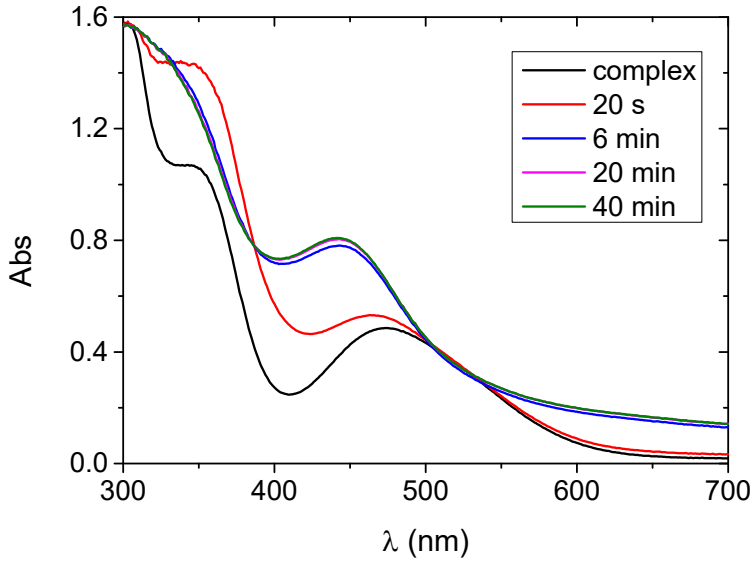
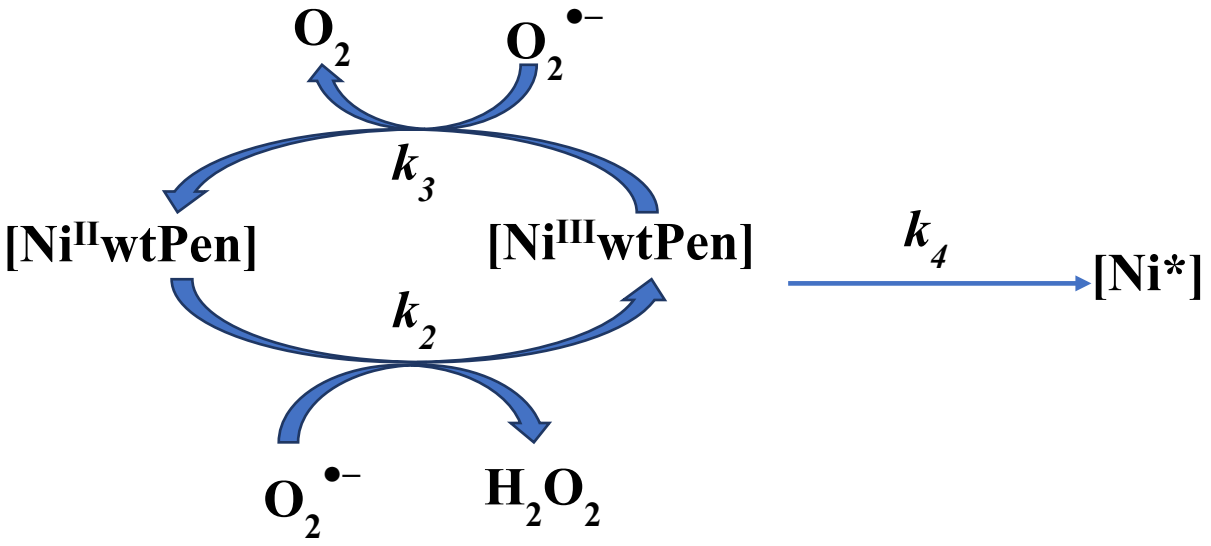


Figure S14. UV-Vis spectra recorded in the Ni/**wtPen**: H_2O_2 1:1:0.9 system at pH 7.6 as a function of time. $c_{complex}$ = 2 mM

Catalytic activity.



Scheme S1. Postulated kinetic model of the dismutation reaction and the kinetically coupled degradation of the Ni^{III} complex.

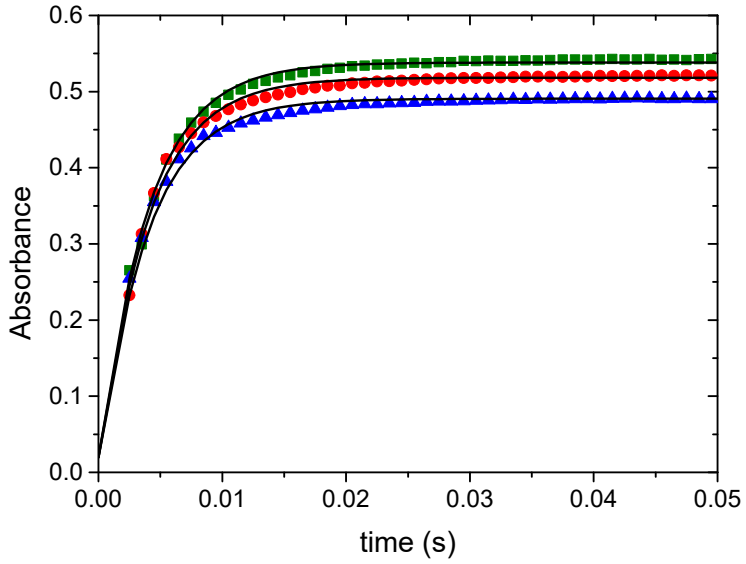


Figure S15. Kinetic traces recorded in the presence of Ni(**wtPen**) complex at comparable concentrations of superoxide anion. $c(\text{complex})^0$ = 0.21 mM; $c(O_2^{\bullet-})^0$ = 0.43 mM (blue), 0.88 mM (red) and 1.30 mM (green). Solid lines represent the fitted kinetic traces on the basis of

the proposed kinetic model. Solvent 1:1 aqueous HEPES buffer (50 mM, pH 7.6) / DMSO mixture. λ = 376 nm, l = 10 mm.

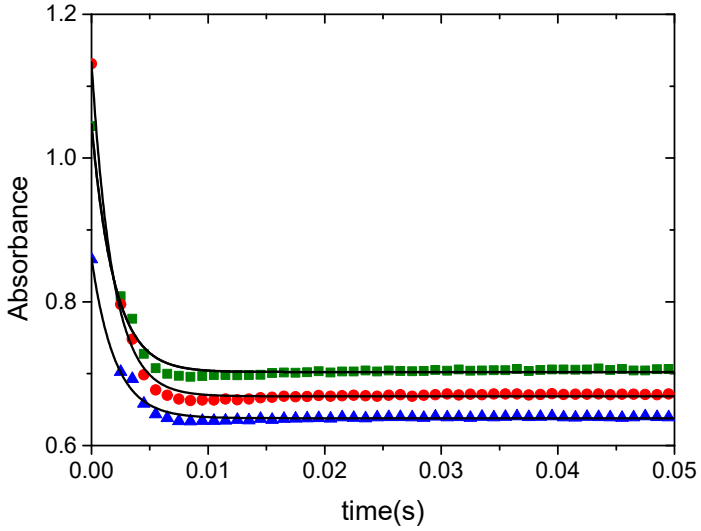


Figure S16. Kinetic traces recorded in the presence of Ni(**wtNiSOD**) complex at comparable concentrations of superoxide anion. c(complex)^0 = 0.20 mM; $c(O_2^-)^0$ = 0.51 mM (blue), 0.86 mM (red) and 1.02 mM (green). Solid lines represent the fitted kinetic traces on the basis of the proposed kinetic model. Solvent 1:1 aqueous HEPES buffer (50 mM, pH 7.6) / DMSO mixture. λ = 260 nm, l = 2 mm.

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