ELECTRONIC SUPPLEMENTARY INFORMATION

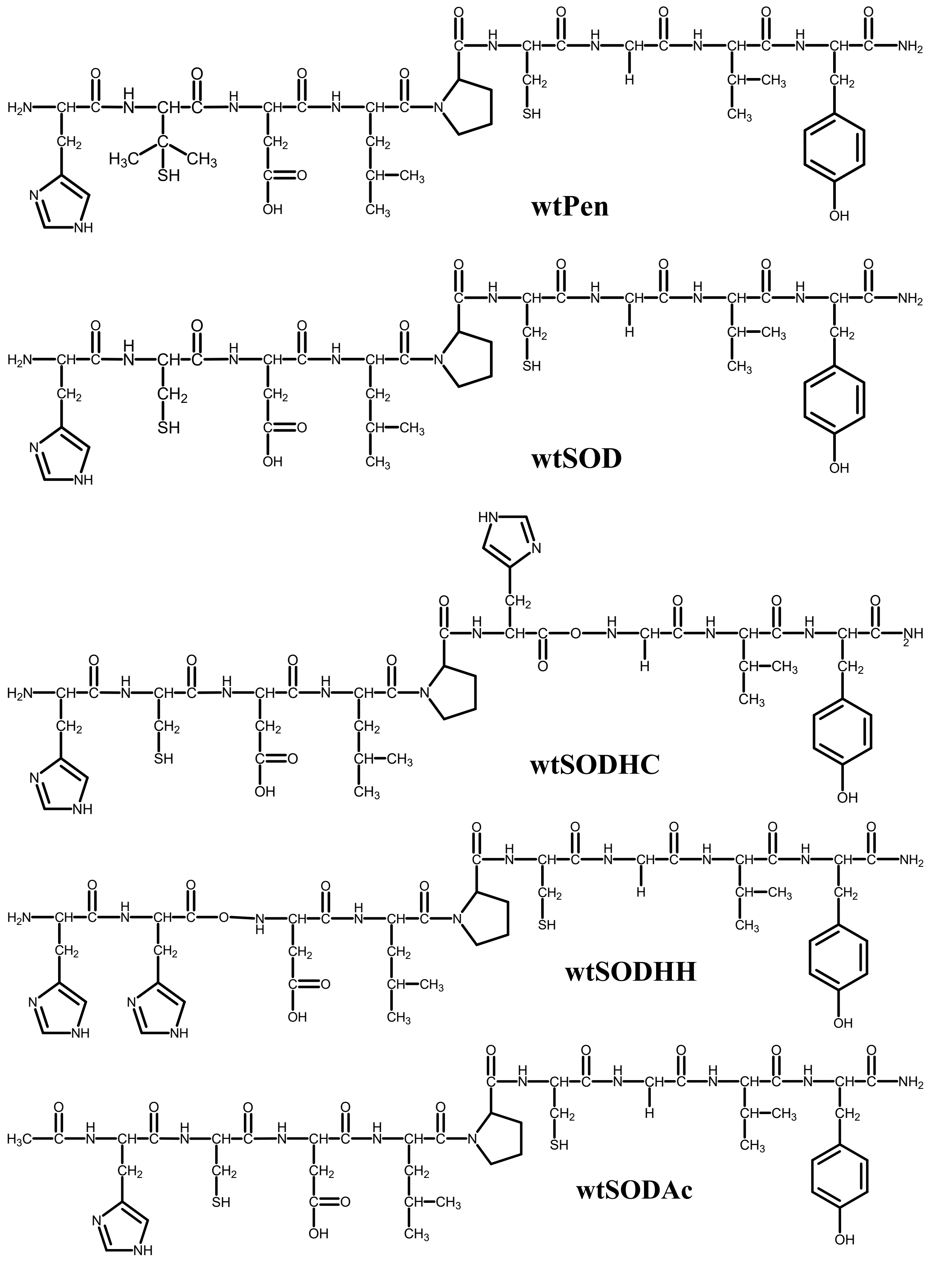
The role of the terminal cysteine moiety in a metallopeptide mimicking the active site of the NiSOD enzyme

Dóra Bonczidai-Kelemen, [a, b] *Klaudia Tóth,*[a] *I. Fábián,* [a] *N. Lihi* [a] *

[a] HUN-REN–UD Mechanisms of Complex Homogeneous and Heterogeneous Chemical Reactions Research Group, Department of Inorganic and Analytical Chemistry, Faculty of Science and Technology, University of Debrecen, H-4032 Debrecen, Hungary

[b] Doctoral School of Chemistry, University of Debrecen, Debrecen H-4032, Hungary

Corresponding author. lihi.norbert@science.unideb.hu (N.L.).



Scheme S1. Structural formulae of NiSOD related peptides.

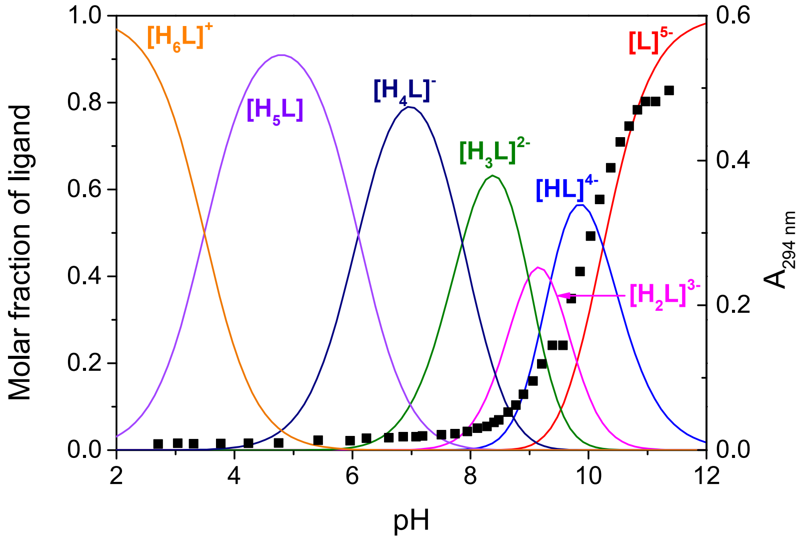


Figure S1. Concentration distribution curves and the absorbance at 294 nm as a function of pH recorded in the H^+/**wtCC** system. $c_{\mathbf{wtCC}}$ = 0.99 mM, I = 0.2 M KCl, T = 25 °C, l = 2 mm.

$$c_{Ni(II)} = [Ni(II)] + \sum_{i=1}^{n} p\beta_{pqr}[Ni(II)]_i^p[wtCC]_i^r[H^+]_i^q \qquad \text{(S1)}$$

$$c_{wtCC} = [wtCC] + \sum_{i=1}^{n} r\beta_{pqr}[Ni(II)]_i^p[wtCC]_i^r[H^+]_i^q \qquad \text{(S2)}$$

$$c_{H^+} = [H^+] + \sum_{i=1}^{n} q\beta_{pqr}[Ni(II)]_i^p[wtCC]_i^r[H^+]_i^q \qquad \text{(S3)}$$

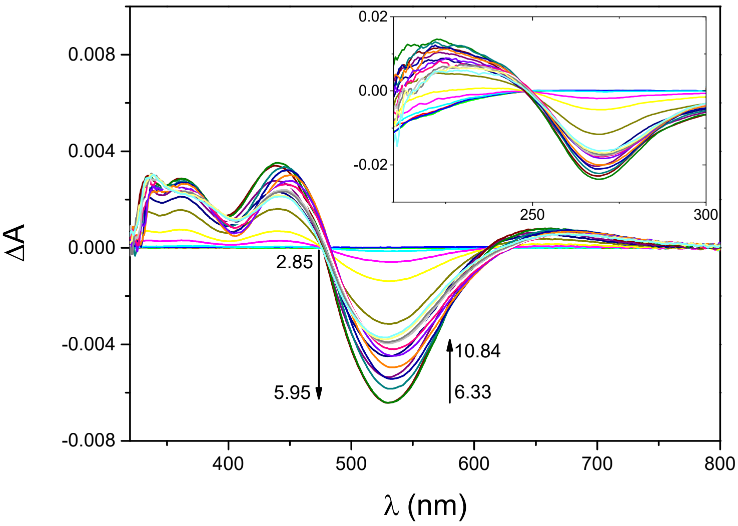
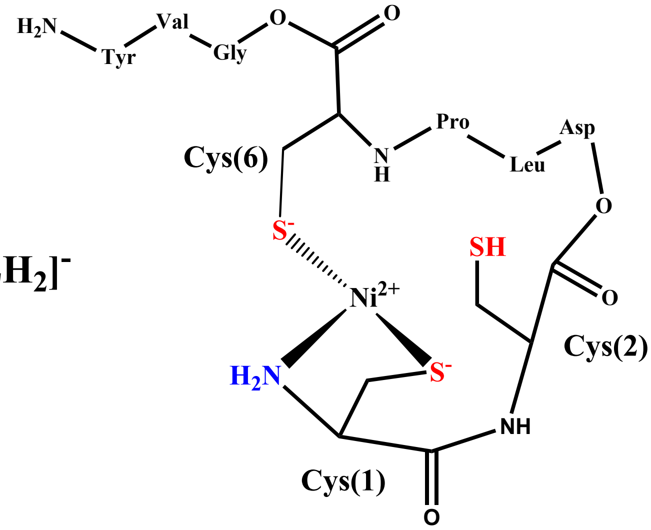
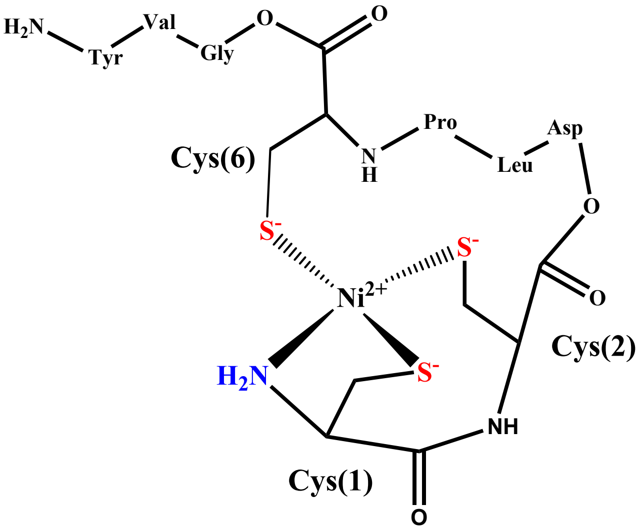


Figure S2. pH-dependent CD spectra recorded in the Ni(II)/**wtCC** system at 0.9:1 metal to ligand ratio. $c_{\mathbf{wtCC}}$ = 1.11 mM, $c_{\mathrm{Ni(II)}}$ = 1.04 mM, I = 0.2 M KCl, T = 25 °C, l = 1 mm.

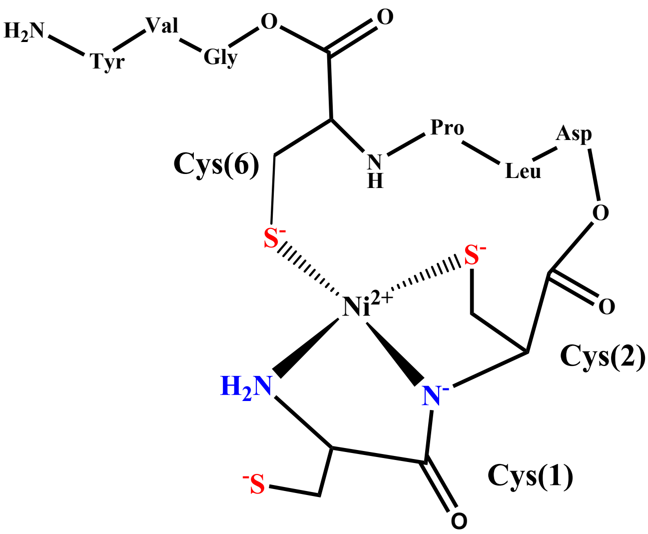
[NiLH$_2$]$^-$



[NiLH]$^{2-}$



[NiL]$^{3-}$



Scheme S2. Postulated binding modes of the complexes formed in the Ni(II)/**wtCC** system.

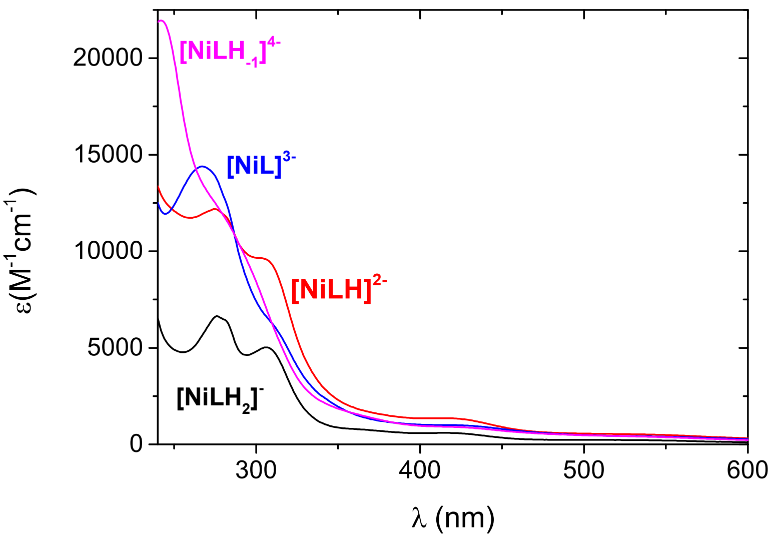


Figure S3. Calculated individual spectra of the complexes formed in the Ni(II)/**wtCC** system.

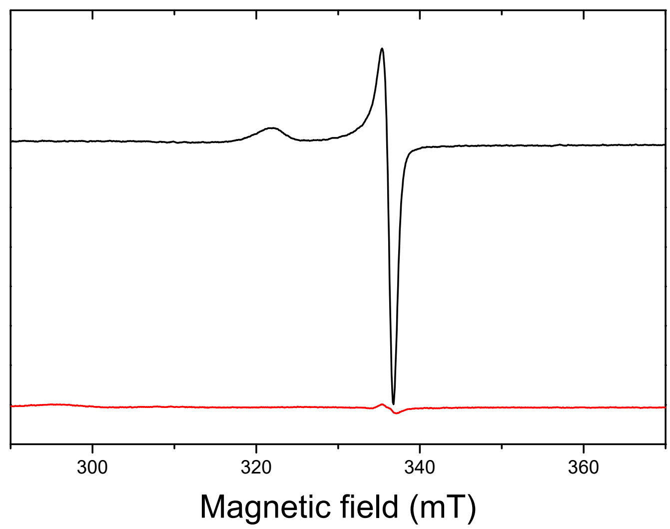


Figure S4. Frozen solution CW-EPR spectrum of KO_2 (black) and the spectrum recorded after the addition of the Ni/**wtCC** system at pH 10.0 (red). The spectra were recorded at 77 K.

$$2\,H^+ + 2\,O_2^- \rightarrow H_2O_2 + O_2 \qquad k_1 \qquad \text{(S4)}$$ k_1

$$Ni^{II}L + 2\,H^+ + O_2^- \rightarrow Ni^{III}L + H_2O_2 \qquad k_2 \qquad \text{(S5)}$$

$$Ni^{III}L + O_2^- \rightarrow Ni^{II}L + O_2 \qquad k_3 \qquad \text{(S6)}$$

$$Ni^{III}L \rightarrow Ni^*L \qquad k_4 \qquad \text{(S7)}$$

$$\frac{d[O_2^-]}{dt} = -\,k_1 \times [O_2^-]^2 - k_2 \times [Ni^{II}L][O_2^-] - k_3 \times [Ni^{III}L][O_2^-] \qquad \text{(S8)}$$

$$\frac{d[H_2O_2]}{dt} = k1 \times [O_2^-]^2 + k_2 \times [Ni^{II}L][O_2^-] \qquad \text{(S9)}$$

$$\frac{d[Ni^{II}L]}{dt} = -k_2 \times [Ni^{II}L][O_2^-] + k_3 \times [Ni^{III}L][O_2^-] \qquad \text{(S10)}$$

$$\frac{d[Ni^{III}L]}{dt} = k_2 \times [Ni^{II}L][O_2^-] - k_3 \times [Ni^{III}L][O_2^-] - k_4 \times [Ni^*L] \qquad \text{(S11)}$$

$$\frac{d[Ni^*L]}{dt} = k_4 \times [Ni^{III}L] \qquad \text{(S12)}$$

$$Abs = \varepsilon_{Ni(II)} \times [Ni^{II}L] + \varepsilon_{Ni(III)} \times [Ni^{III}L] + \varepsilon_{Ni*} \times [Ni^*L] + \varepsilon_{O_2^-} \times [O_2^-] + \varepsilon_{H_2O_2} \times [H_2O_2] \qquad \text{(S13)}$$

Table S1. Kinetic parameters of the reaction between superoxide anion and Ni(II)/**wtCC** system at different pH values.

	pH = 7.6	pH = 7.8	pH = 8.1	Unit
k_2	$(6.6 \pm 0.6) \times 10^7$	$(2.6 \pm 0.2) \times 10^7$	$(1.1 \pm 0.2) \times 10^7$	$M^{-1}s^{-1}$
k_3	$(1.6 \pm 0.4) \times 10^8$	$(1.8 \pm 0.1) \times 10^8$	$(1.7 \pm 0.2) \times 10^8$	$M^{-1}s^{-1}$
k_4	1310 ± 90	842 ± 4	801 ± 6	s^{-1}