SUPPLEMENTARY INFORMATION

FOR

Are thiophenol based small molecular weight nickel complexes sufficient mimics of the NiSOD enzyme?

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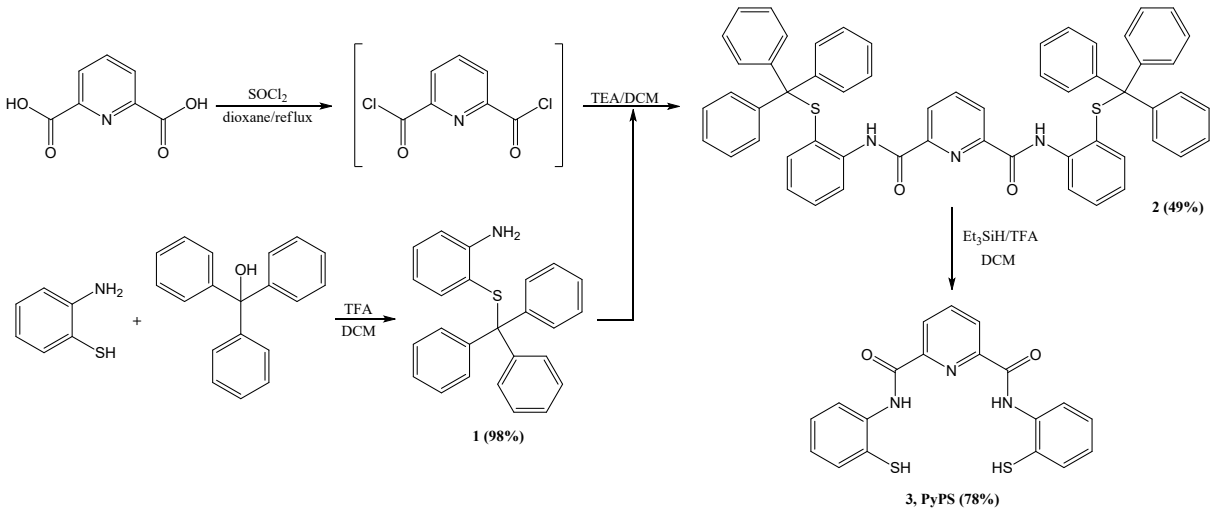


Scheme S1. The outline of the synthesis of PyPS.

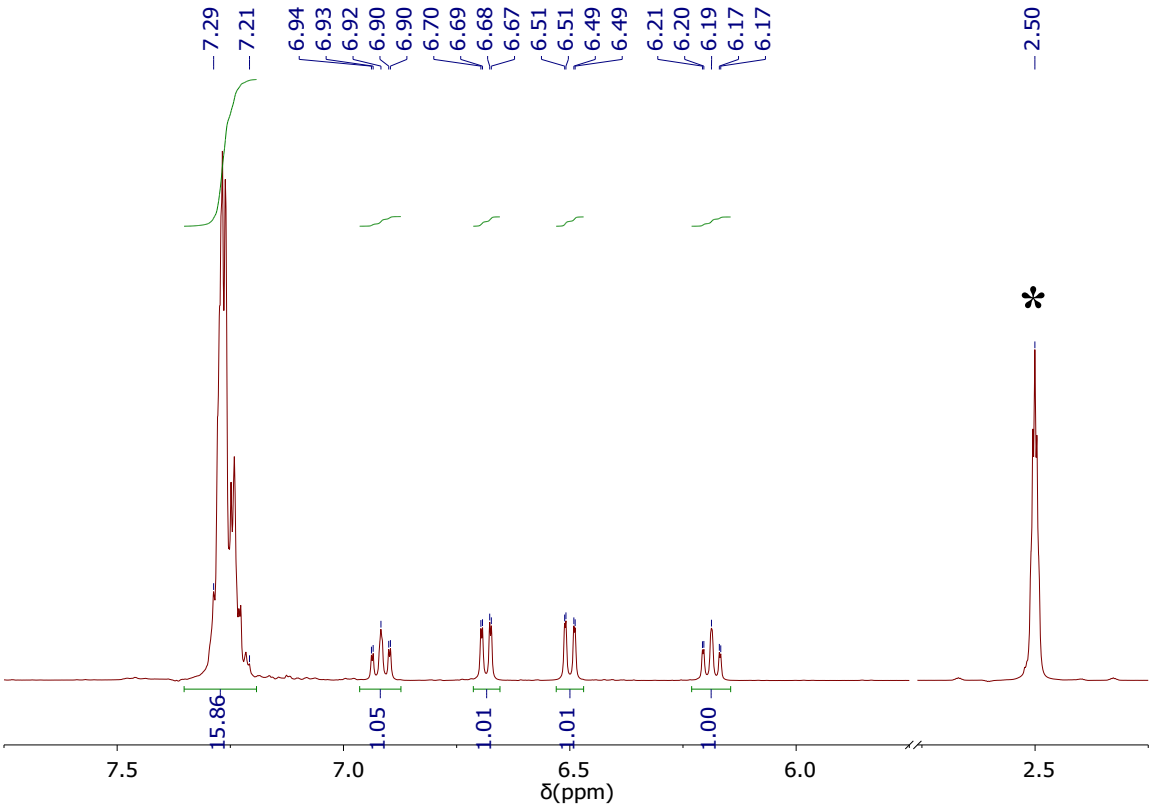


Figure S1. ^{1}H NMR spectrum of 2-(tritylthio)aniline in DMSO-d_6. The solvent residual peak is indicated by *.

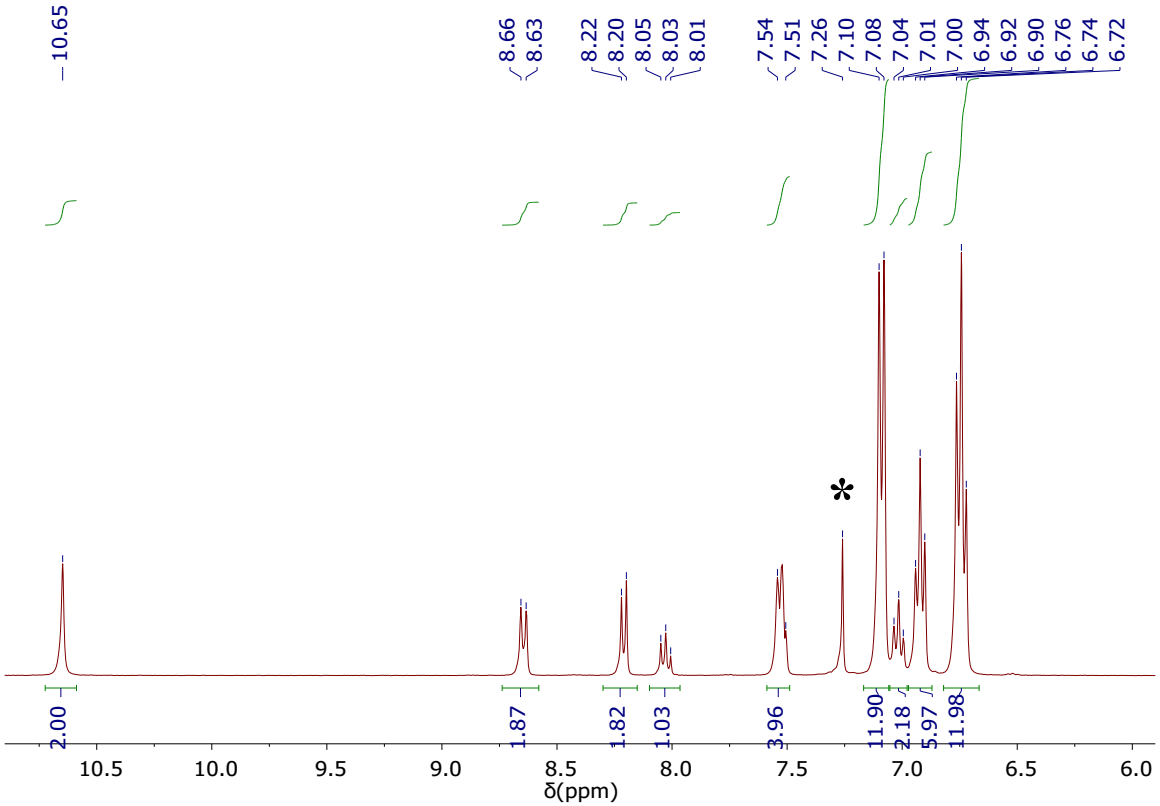


Figure S2. ^{1}H NMR spectrum of PyPS-Trt in $CDCl_3$. The solvent residual peak is indicated by *.

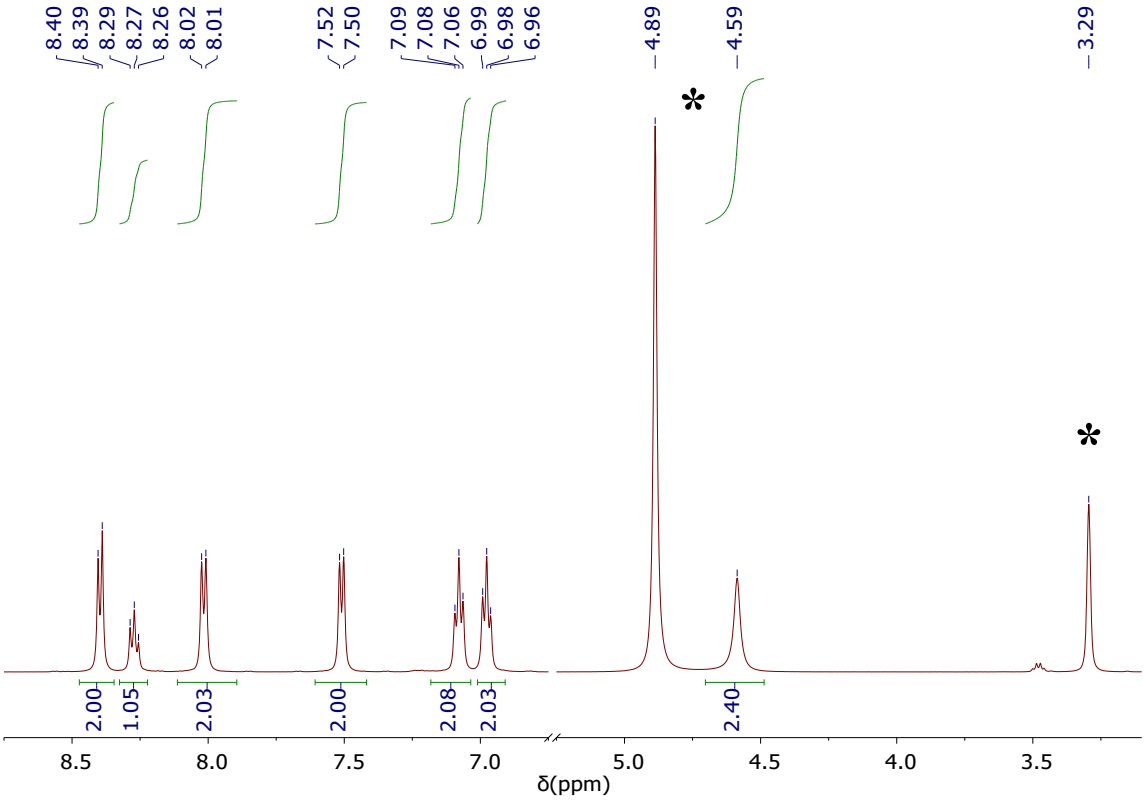


Figure S3. ^{1}H NMR spectrum of PyPS in MeOD. The solvent residual peak is indicated by *.

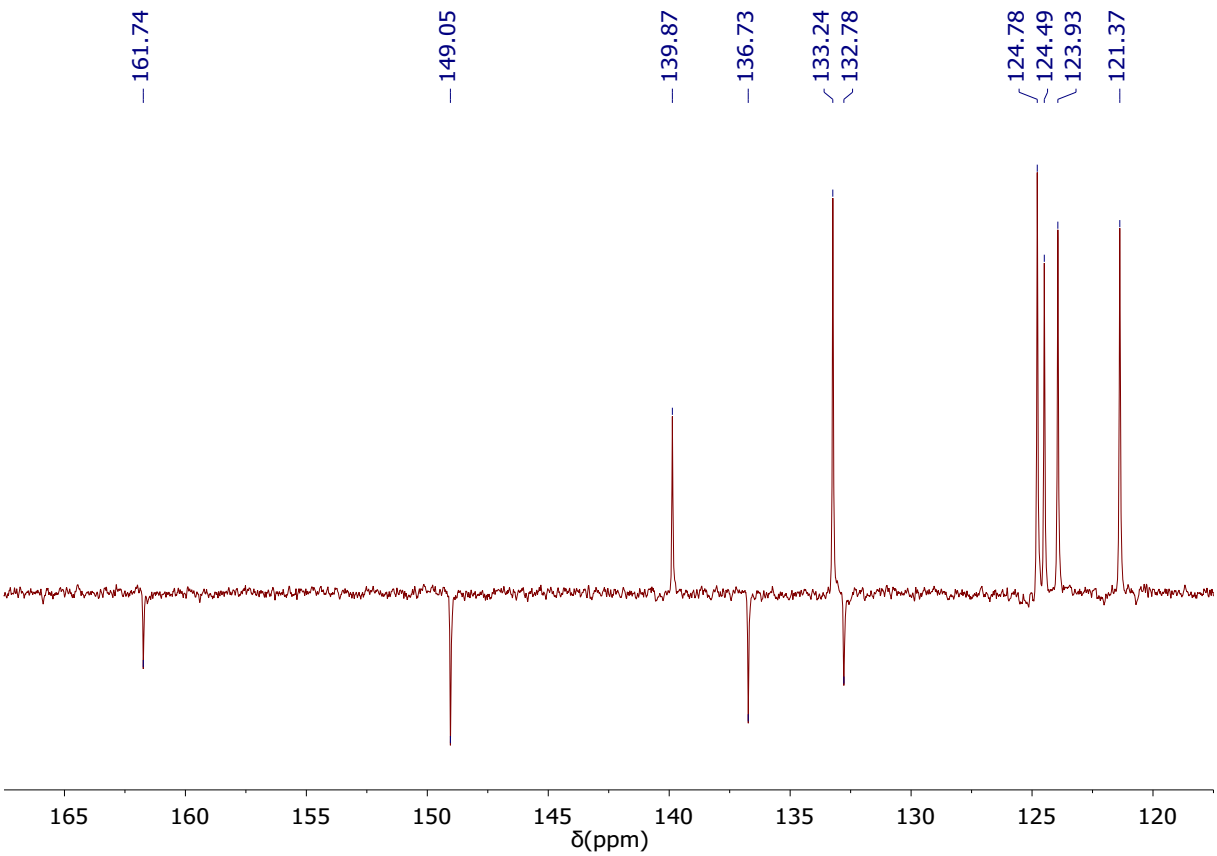


Figure S4. ^{13}C NMR spectrum of PyPS in MeOD.

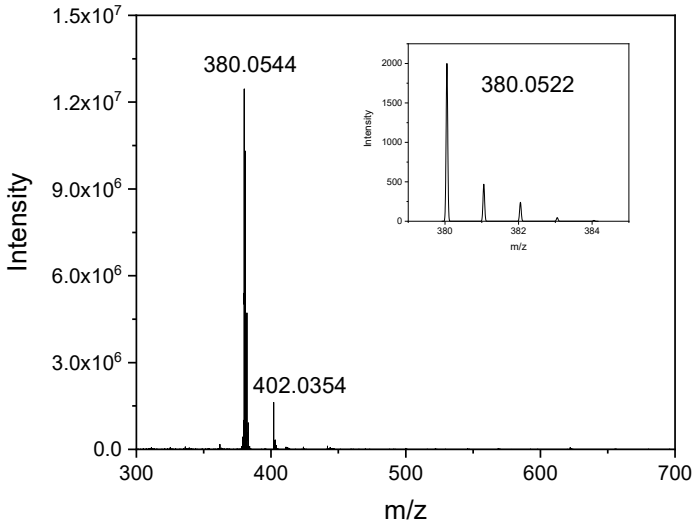
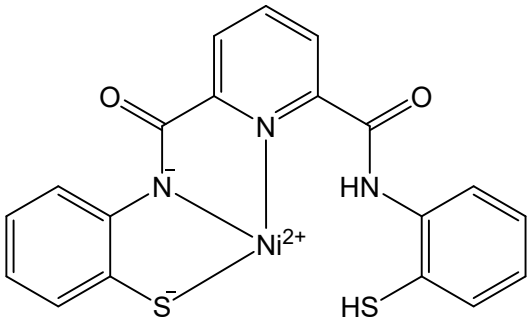
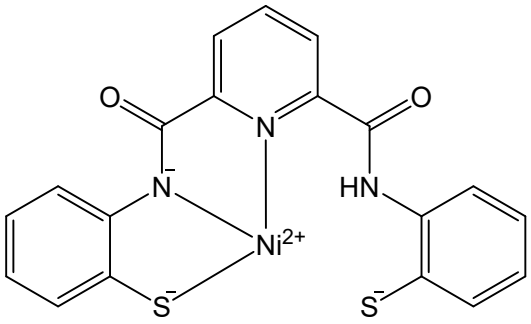


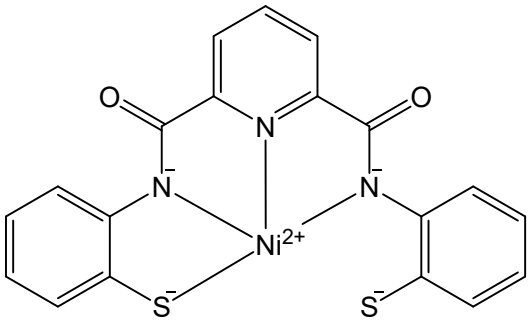
Figure S5. Mass spectrum of PyPS. Inset: Calculated isotope pattern of PyPS with $[C_{19}H_{14}N_3O_2S_2]^-$ stoichiometry.



[NiPyPS]



[NiPyPSH$_{-1}$]$^{-}$



[NiPyPSH$_{-2}$]$^{2-}$

Scheme S2. Proposed coordination modes of the complexes formed in the Ni(II)/PyPS system.

Table S1. Crystal data and structure refinement parameters.

Identification code	nipypsh4_I2pa
Empirical formula	$C_{84}H_{46}N_{12}Na_4Ni_4O_{15}S_8$
Moiety formula	$C_{76}H_{46}N_{12}Na_4Ni_4O_{13}S_8$, 2($C_4O$)
Formula weight	2046.634
Temperature/K	103.00
Crystal system	monoclinic
Space group	I2/a
a/Å	16.4372(18)
b/Å	18.2654(8)
c/Å	33.6006(8)
α/°	90

β/°	95.115(8)
γ/°	90
Volume/Å^3	10047.8(12)
Z/ Z'	4/0.5
ρ_{calc}g/cm^3	1.353
μ/mm^{-1}	0.984
F(000)	4164.8
Crystal size/mm^3	0.5 × 0.3 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.14 to 50.7
Index ranges	-19 ≤ h ≤ 19, -21 ≤ k ≤ 21, -40 ≤ l ≤ 40
Reflections collected	192190
Independent reflections	9169 [R_{int} = 0.1408, R_{sigma} = 0.0467]
Data/restraints/parameters	9169/236/633
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.1074, wR_2 = 0.2218
Final R indexes [all data]	R_1 = 0.1207, wR_2 = 0.2290
Largest diff. peak/hole / e Å^{-3}	1.39/-0.76

Table S2. Atomic occupancy for the nickel(II)/PyPS complex.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
Na3	0.500000	H6a	0.500000	H6b	0.500000
O9	0.500000	O8	0.500000	O5	0.482(18)
C1a	0.482(18)	C1b	0.482(18)	C1c	0.482(18)
C1d	0.482(18)	C1e	0.518(18)	C39	0.518(18)
O5a	0.518(18)	C1f	0.518(18)	C1g	0.518(18)

Table S3. Solvent masks information for the nickel(II)/PyPS complex.

Number	X	Y	Z	Volume	Electron count
1	0.250	0.182	0.500	162.4	5.4
2	0.250	0.318	0.000	162.4	5.4
3	-0.250	0.682	1.000	162.4	5.4
4	-0.250	0.818	0.500	162.4	5.4

Number	X	Y	Z	Volume	Electron count
5	0.217	0.008	0.717	58.4	2.4
6	0.217	0.492	0.217	58.4	2.4
7	0.250	0.697	0.000	29.1	0.6
8	0.250	0.803	0.500	29.1	0.6
9	0.283	0.492	0.783	58.4	2.2
10	0.283	0.008	0.283	58.4	2.2
11	0.717	0.508	0.217	58.4	2.4
12	0.717	0.992	0.717	58.4	2.4
13	0.750	0.197	0.500	29.1	0.6
14	0.750	0.303	0.000	29.1	0.6
15	0.783	-0.008	0.283	58.4	2.2
16	0.783	0.508	0.783	58.4	2.2

Table S4. Bond lengths for the nickel(II)/PyPS complex.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	S1	2.148(2)	C14	C19	1.396(11)
Ni1	N2	1.828(6)	C17	C18	1.374(11)
Ni1	N3	1.921(6)	C17	C16	1.380(12)
Ni1	N1	1.866(7)	C13	C12	1.485(11)
Ni2	S3	2.146(2)	C12	C11	1.373(11)
Ni2	N6	1.857(7)	C15	C16	1.390(12)
Ni2	N5	1.822(7)	C7	C8	1.489(12)
Ni2	N4	1.906(7)	C6	C1	1.392(11)
S1	Na2[1]	3.359(2)	C6	C5	1.361(12)
S1	C1	1.768(8)	C27	C26	1.509(13)
S2	S4	2.034(3)	C27	C28	1.376(12)
S2	C19	1.783(8)	C8	C9	1.374(11)
S3	C20	1.770(9)	C1	C2	1.395(12)
S4	Na3	3.195(10)	C31	C30	1.355(12)
S4	C38	1.791(9)	C31	C32	1.500(12)
Na1	Na32	3.359(10)	C33	C38	1.392(11)
Na1	O2	2.240(7)	C33	C34	1.372(12)
Na1	O33	2.212(7)	C10	C9	1.410(13)
Na1	O42	2.227(8)	C10	C11	1.383(12)
Na1	O7	2.252(9)	C37	C38	1.370(12)
Na2	O1	2.175(6)	C37	C36	1.377(12)
Na2	O14	2.175(6)	C18	C19	1.395(11)
Na2	O6	2.259(14)	C29	C30	1.379(13)
Na3	O32	2.561(13)	C29	C28	1.389(13)
Na3	O4	2.745(13)	C35	C34	1.388(13)
Na3	O9	2.13(2)	C35	C36	1.393(12)
Na3	O8	2.23(2)	C2	C3	1.375(13)
O1	C13	1.234(9)	C20	C25	1.399(12)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C7	1.230(10)	C20	C21	1.365(13)
O3	C26	1.244(11)	C25	C24	1.396(13)
O4	C32	1.231(11)	C5	C4	1.389(13)
N2	C12	1.322(10)	C21	C22	1.383(14)
N2	C8	1.342(10)	C22	C23	1.367(16)
N6	C26	1.342(11)	C3	C4	1.389(14)
N6	C25	1.426(11)	C24	C23	1.377(14)
N3	C14	1.432(10)	O5	C1b	1.413(15)
N3	C13	1.333(10)	O5	C1c	1.423(15)
N1	C7	1.360(10)	C1a	C1b	1.468(16)
N1	C6	1.430(10)	C1c	C1d	1.474(15)
N5	C27	1.313(11)	C1e	C39	1.48(3)
N5	C31	1.337(11)	C39	O5a	1.42(3)
N4	C33	1.435(11)	O5a	C1f	1.46(3)
N4	C32	1.331(11)	C1f	C1g	1.42(3)
C14	C15	1.367(11)			

[1]-X,-Y,-Z; [2]-X,-1/2+Y,1/2-Z; [3]+X,-1+Y,+Z; [4]1/2-X,+Y,-Z

Table S5. Bond angles for the nickel(II)/PyPS complex.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	Ni1	S1	171.5(2)	C32	N4	Ni2	115.4(6)
N3	Ni1	S1	104.1(2)	C32	N4	C33	118.8(7)
N3	Ni1	N2	82.0(3)	C15	C14	N3	121.0(7)
N1	Ni1	S1	90.0(2)	C19	C14	N3	119.3(7)
N1	Ni1	N2	83.9(3)	C19	C14	C15	119.7(7)
N1	Ni1	N3	165.9(3)	C16	C17	C18	120.7(8)
N6	Ni2	S3	90.6(2)	N3	C13	O1	127.5(7)
N5	Ni2	S3	173.6(2)	C12	C13	O1	120.9(7)
N5	Ni2	N6	83.7(3)	C12	C13	N3	111.6(7)
N4	Ni2	S3	103.2(2)	C13	C12	N2	111.4(7)
N4	Ni2	N6	166.3(3)	C11	C12	N2	119.5(8)
N4	Ni2	N5	82.7(3)	C11	C12	C13	129.1(8)
Na21	S1	Ni1	112.56(9)	C16	C15	C14	120.2(8)
C1	S1	Ni1	96.8(3)	N1	C7	O2	127.7(8)
C1	S1	Na21	88.4(3)	C8	C7	O2	121.9(8)
C19	S2	S4	103.4(3)	C8	C7	N1	110.4(7)
C20	S3	Ni2	96.7(3)	C1	C6	N1	113.9(7)
Na3	S4	S2	117.5(2)	C5	C6	N1	125.5(8)
C38	S4	S2	104.6(3)	C5	C6	C1	120.7(8)
C38	S4	Na3	113.2(3)	C26	C27	N5	110.9(7)
O2	Na1	Na32	98.6(3)	C28	C27	N5	121.8(9)
O33	Na1	Na32	49.7(3)	C28	C27	C26	127.3(8)
O33	Na1	O2	111.7(3)	C7	C8	N2	112.0(7)
O42	Na1	Na32	54.4(3)	C9	C8	N2	119.8(8)
O42	Na1	O2	104.6(3)	C9	C8	C7	128.1(8)
O42	Na1	O33	98.2(3)	C6	C1	S1	119.3(6)
O7	Na1	Na32	150.4(3)	C2	C1	S1	121.9(7)
O7	Na1	O2	104.9(3)	C2	C1	C6	118.7(8)
O7	Na1	O33	103.9(3)	C30	C31	N5	120.2(9)
O7	Na1	O42	133.0(4)	C32	C31	N5	109.9(7)
S14	Na2	S11	153.6(2)	C32	C31	C30	129.8(8)
O1	Na2	S11	92.12(17)	C38	C33	N4	119.7(8)
O1	Na2	S14	78.00(16)	C34	C33	N4	120.4(8)
O15	Na2	S11	78.00(16)	C34	C33	C38	119.9(8)
O15	Na2	S14	92.12(17)	C11	C10	C9	119.5(8)
O1	Na2	O15	136.0(4)	N6	C26	O3	128.9(9)
O6	Na2	S14	103.18(10)	C27	C26	O3	120.3(8)
O6	Na2	S11	103.18(10)	C27	C26	N6	110.8(8)
O6	Na2	O1	112.0(2)	C36	C37	C38	120.7(8)
O6	Na2	O15	112.0(2)	C10	C9	C8	118.2(8)
Na16	Na3	S4	101.8(3)	C19	C18	C17	119.1(8)
O32	Na3	S4	108.0(4)	C28	C29	C30	121.0(9)
O32	Na3	Na16	41.2(2)	C36	C35	C34	119.4(9)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O4	Na3	S4	71.4(3)	C10	C11	C12	119.6(8)
O4	Na3	Na16	41.3(2)	C14	C19	S2	116.3(6)
O4	Na3	O32	78.4(3)	C18	C19	S2	123.4(6)
O9	Na3	S4	91.2(9)	C18	C19	C14	120.3(7)
O9	Na3	Na16	128.4(6)	C3	C2	C1	121.3(9)
O9	Na3	O32	159.2(9)	C25	C20	S3	118.9(7)
O9	Na3	O4	101.3(6)	C21	C20	S3	121.4(7)
O8	Na3	S4	93.6(6)	C21	C20	C25	119.6(8)
O8	Na3	Na16	134.9(6)	C33	C38	S4	116.7(6)
O8	Na3	O32	93.8(6)	C37	C38	S4	123.5(7)
O8	Na3	O4	159.5(7)	C37	C38	C33	119.8(8)
O8	Na3	O9	92.7(8)	C35	C34	C33	120.4(8)
C13	O1	Na25	163.2(6)	C29	C30	C31	118.6(9)
C7	O2	Na1	146.3(6)	C15	C16	C17	120.0(8)
Na36	O3	Na17	89.1(3)	N4	C32	O4	126.8(8)
C26	O3	Na17	148.7(7)	C31	C32	O4	120.8(8)
C26	O3	Na36	120.3(7)	C31	C32	N4	112.4(8)
Na3	O4	Na16	84.3(3)	C35	C36	C37	119.8(8)
C32	O4	Na16	163.6(7)	C29	C28	C27	116.5(9)
C32	O4	Na3	104.5(8)	C20	C25	N6	114.2(7)
C12	N2	Ni1	119.0(5)	C24	C25	N6	126.0(9)
C8	N2	Ni1	117.2(6)	C24	C25	C20	119.8(9)
C8	N2	C12	123.5(7)	C4	C5	C6	119.9(9)
C26	N6	Ni2	116.1(6)	C22	C21	C20	119.9(10)
C25	N6	Ni2	119.5(6)	C23	C22	C21	121.2(10)
C25	N6	C26	124.4(8)	C4	C3	C2	118.5(9)
C14	N3	Ni1	126.3(5)	C23	C24	C25	119.6(10)
C13	N3	Ni1	114.9(5)	C3	C4	C5	120.8(9)
C13	N3	C14	118.4(6)	C24	C23	C22	119.7(10)
C7	N1	Ni1	116.0(5)	C1c	O5	C1b	122(3)
C6	N1	Ni1	119.7(5)	C1a	C1b	O5	113(2)
C6	N1	C7	124.2(7)	C1d	C1c	O5	114(2)
C27	N5	Ni2	118.5(6)	O5a	C39	C1e	125(4)
C31	N5	Ni2	119.5(6)	C1f	O5a	C39	120(3)
C31	N5	C27	121.9(7)	C1g	C1f	O5a	107(3)
C33	N4	Ni2	125.7(5)				

[1]-X,-Y,-Z; [2]-X,-1/2+Y,1/2-Z; [3]+X,-1+Y,+Z; [4]1/2+X,-Y,+Z; [5]1/2-X,+Y,-Z; [6]-X,1/2+Y,1/2-Z; [7]+X,1+Y,+Z

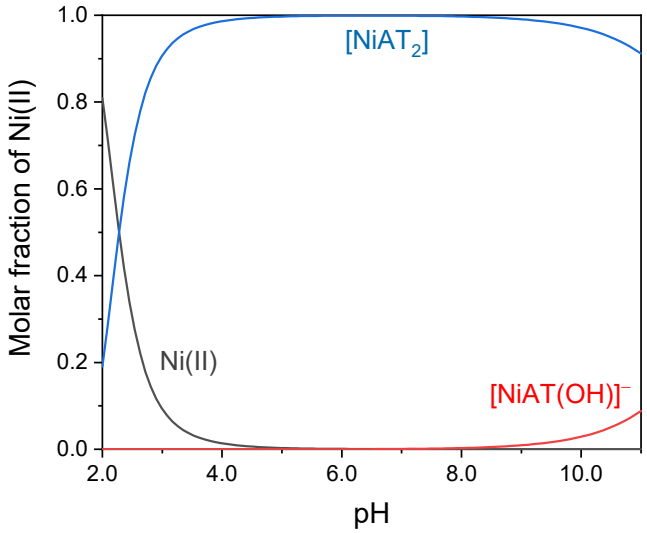


Figure S6. Distribution of the complexes formed in the nickel(II) – 2-aminothiophenol system at 1:2 concentration ratio. $c_{Ni(II)}$ = 0.93 mM, c_{lig} = 1.85 mM

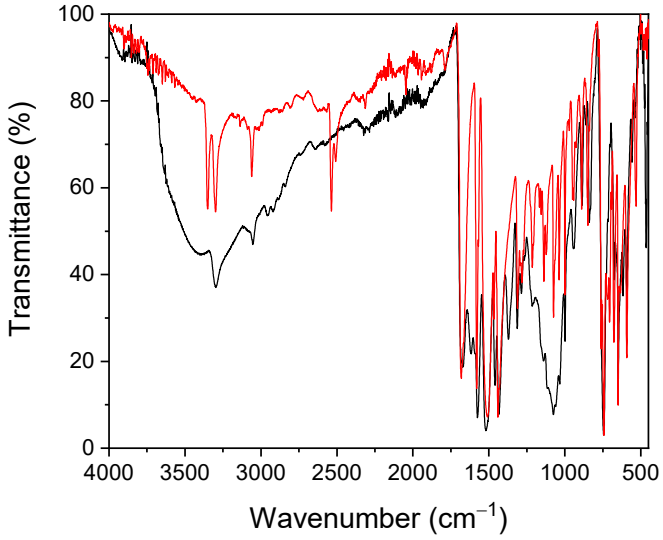


Figure S7. IR spectra of PyPS and its nickel(II) complex.

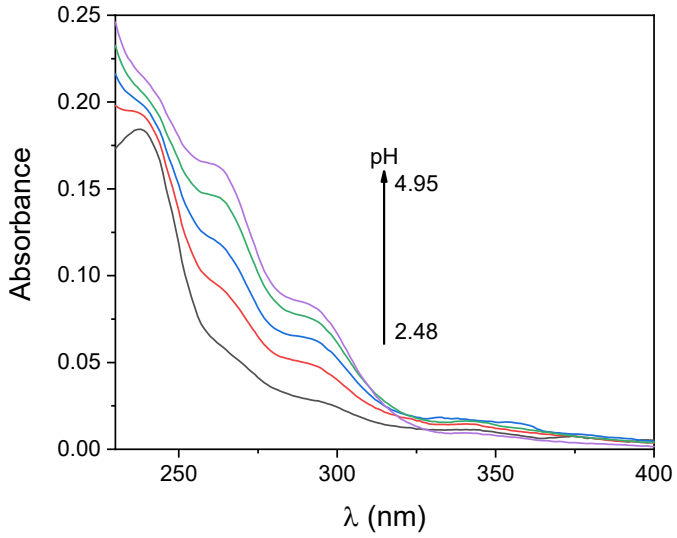


Figure S8. pH dependent UV-Vis spectra recorded in the nickel(II) – AT system at 1:2 concentration ratio. c_{lig} = 49.9 µM, $c_{Ni(II)}$ = 24.3 µM (T = 25 °C and I = 0.2 M KCl)

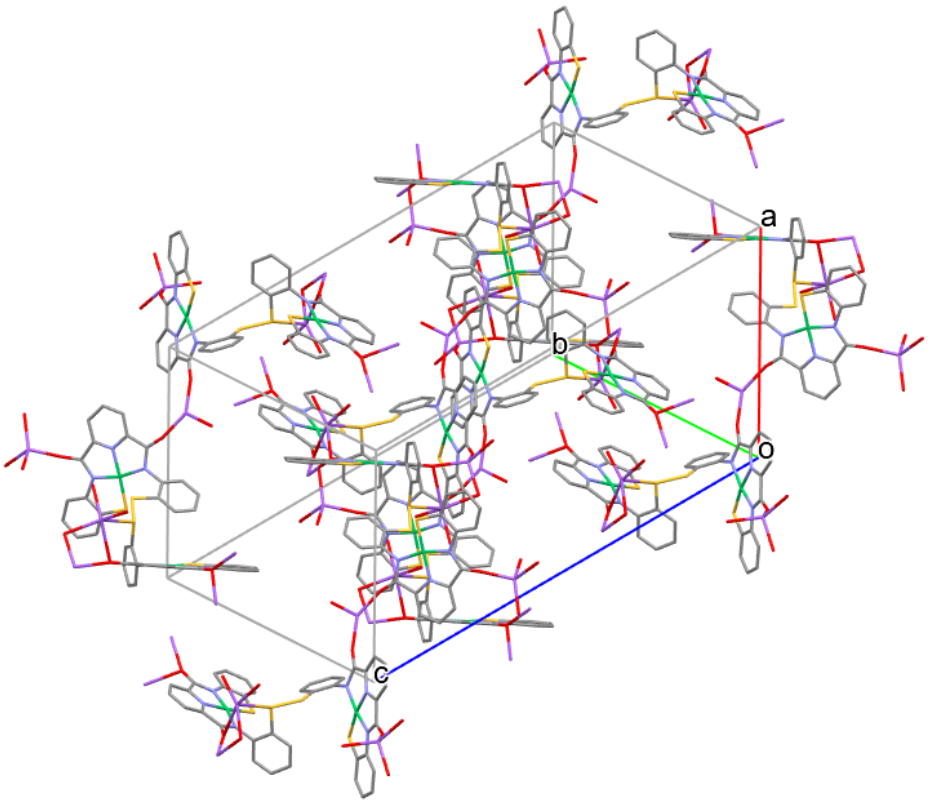


Figure S9. The unit cell of the crystal of the nickel(II) – PyPS complex.

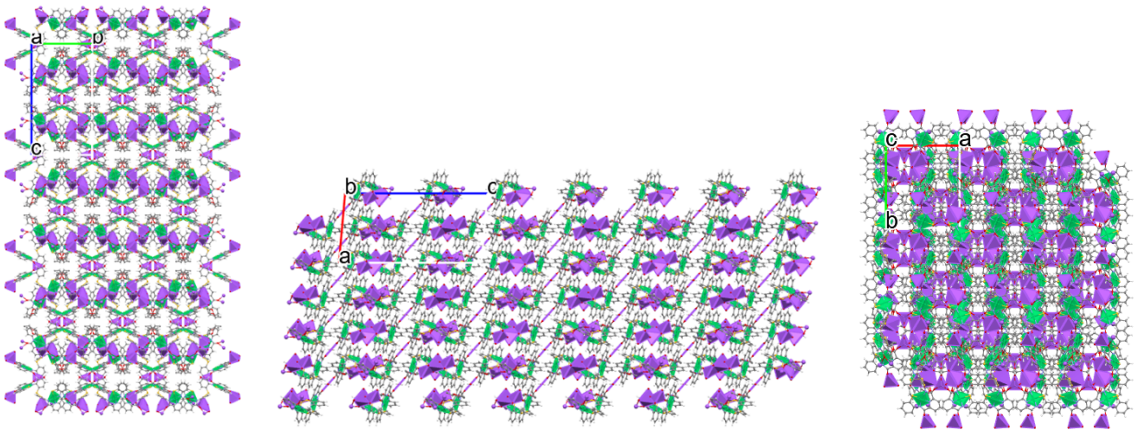


Figure S10. Packing arrangements in the crystal of nickel(II) – PyPS complex viewed from the crystallographic directions 'a', 'b' and 'c'. Purple and green polyhedrons show the coordination sphere of Na^{+} and Ni^{2+} respectively.

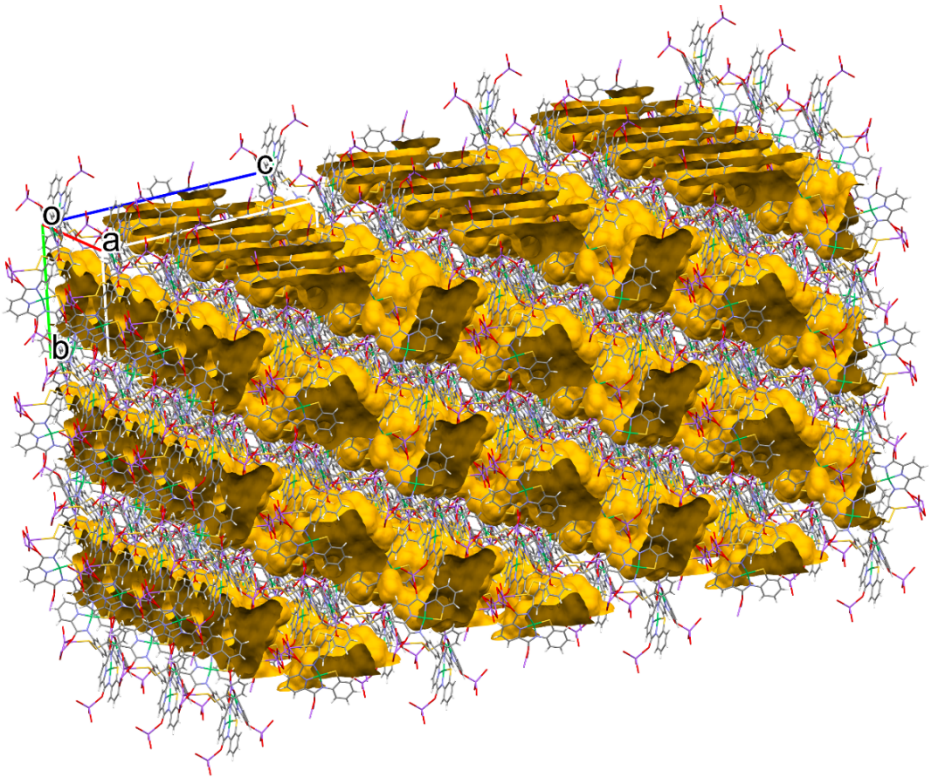
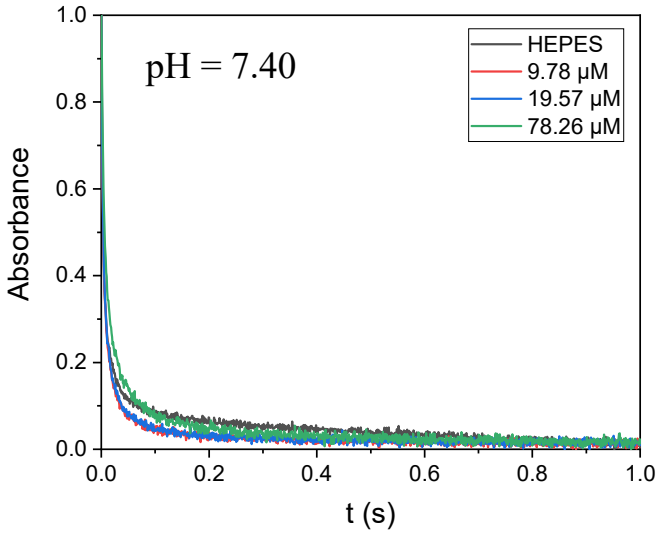
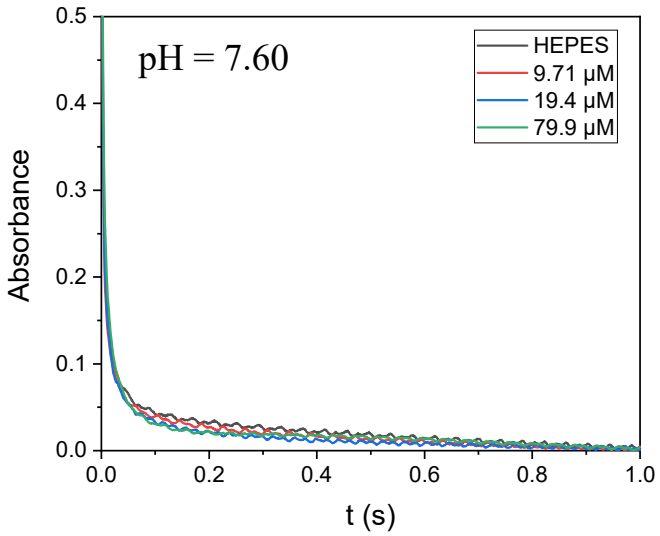
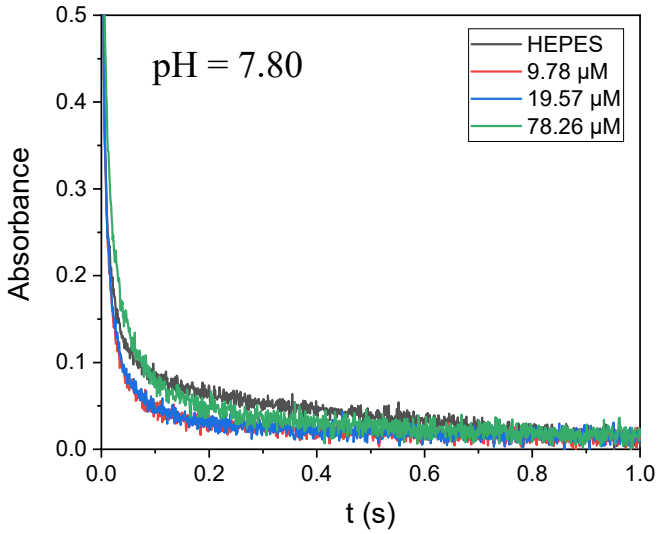
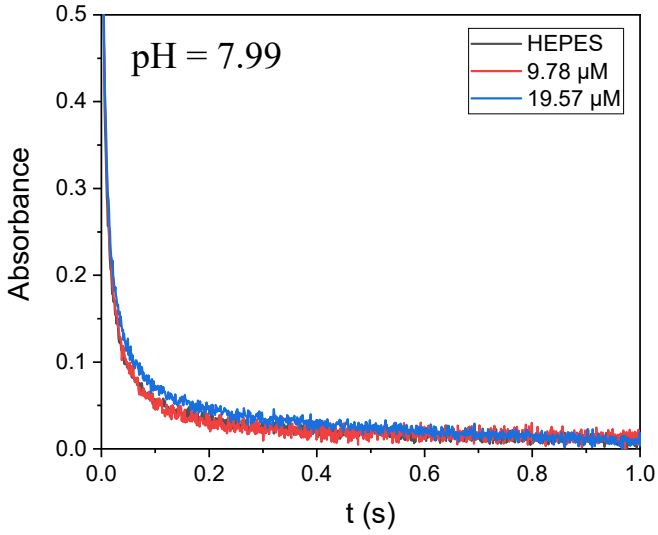


Figure S11. 3D view of the packing arrangements in the crystal of nickel(II) – PyPS complex showing the contact surface of the voids occupied by the disordered ethyl ether solvents coloured by yellow. The void volume is 23.5%, 2361 $Å^3$ of the unit cell.


pH = 7.40
HEPES
9.78 μM
19.57 μM
78.26 μM
Absorbance
t (s)
0.0
0.2
0.4
0.6
0.8
1.0


pH = 7.60
HEPES
9.71 μM
19.4 μM
79.9 μM
Absorbance
t (s)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.8
1.0


pH = 7.80
HEPES
9.78 μM
19.57 μM
78.26 μM
Absorbance
t (s)
0.0
0.1
0.2
0.3
0.4
0.5
0.0
0.2
0.4
0.6
0.8
1.0


pH = 7.99
HEPES
9.78 μM
19.57 μM
Absorbance
t (s)
0.0
0.1
0.2
0.3
0.4
0.5
0.0
0.2
0.4
0.6
0.8
1.0

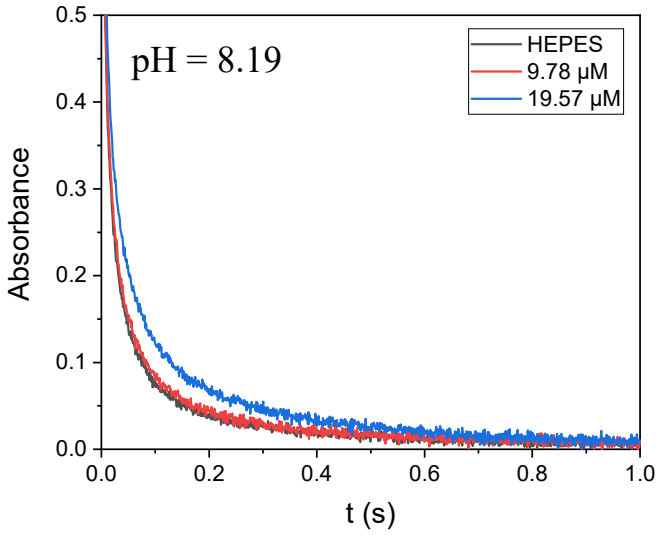


Figure S12. pH dependent kinetic traces recorded for the reaction between superoxide anion and Ni(II) – PyPS complex in HEPES (50 mM) / DMSO 1:1 solvent mixture. $c(O_2^{-})^0$ = 600 μM, λ = 260 nm, T = 25 °C, l = 0.2 cm. The kinetic traces were normalized for better comparison.

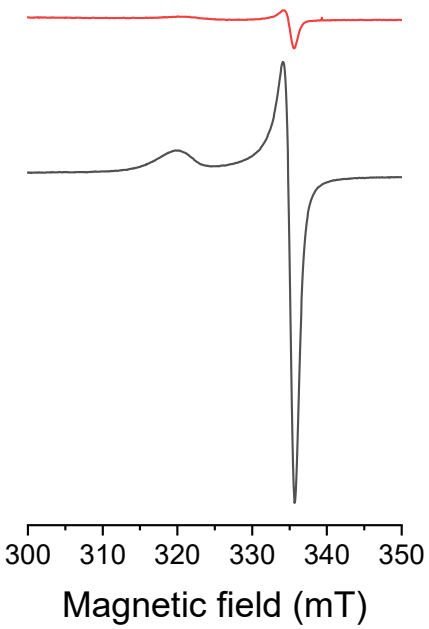


Figure S13. The EPR spectra of KO_2 before (black) and after addition of the nickel(II) – PyPS complex (red). The spectra were recorded in DMSO/water 20/80 solvent mixture at pH 7.6 (HEPES, 50 mM)

Table S6. The metal to ligand ratios and the component ratios obtained by the simulation of frozen solution Ni(III) EPR spectra.[a]

	c_{Ni}/c_{AT}	Component 1 (%)	Component 2 (%)	Component 3 (%)	KO_2 (%)
1	1:4	47	13	40	0
2	1:2	60	20	0	20
3	1:1	78	21	0	0
4	3:2	56	14	30	0

[a] $c^0_{Ni(II)}$ = 2 mM

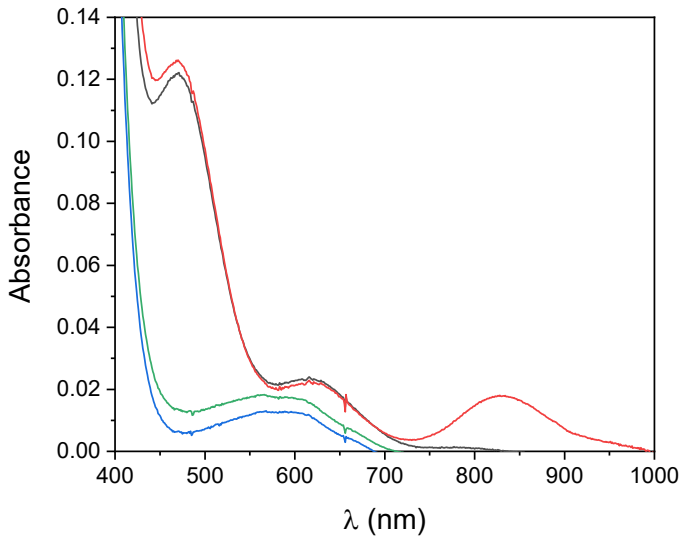


Figure S14. UV-vis spectra recorded in the nickel(II) – AT system before (black) and after the addition of KO_2 (red) and the zinc(II) – AT 1:2 system before (blue) and after the addition of KO_2 (green) at 1:2 metal to ligand concentration ratio in acetonitrile solvent. c_{AT} = 3.00 mM, $c_{Ni(II)} = c_{Zn(II)}$ = 1.50 mM (T = 25 °C)