Supporting Information

N₃-ligated Nickel(II) Diketonate Complexes: Synthesis, Characterization and Evaluation of O₂ Reactivity

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Table of Contents:

Figure S1-S4: Paramagnetic ¹ H NMR of crystallized complexes 1-4	S4-S7
Figure S5-S7: Paramagnetic ¹ H NMR of the filtrate and precipitate of 1-3	S8-S10
Figure S8-S11: ESI-MS of complexes 1-4	S11-S14
Figure S12-S15: UV-Vis absorption spectra of 1-4	
Figure S16-S19: IR spectra of 1-4	
Figure S20: Paramagnetic ¹ H NMR of the precipitate of 5	\$23
Figure S21: Paramagnetic ¹ H NMR of the filtrate of 5	\$24
Figure S22: Paramagnetic ¹ H NMR of the precipitate of 6	\$25
Figure S23: Paramagnetic ¹ H NMR of the filtrate of 6	S26
Figure S24-S25: ESI-MS of the filtrate and precipitate of 5-6	S27-S28
Figure S26: Paramagnetic ¹ H NMR of crystallized complex 8 in CD ₃ CN	\$29
Figure S27: Paramagnetic ¹ H NMR of crystallized complex 8 in DMSO-d ₆	
Figure S28: ESI-MS of complex 8	S31
Figure S29: UV-Vis absorption spectra of 8	S32
Figure S30: IR spectra of 8	
Figure S31: Paramagnetic ¹ H NMR of the precipitate of 6 formed following published pro	oceduresS34
Figure S32: ESI-MS of the precipitate of 6 formed following published procedures	\$35
Figure S33: Paramagnetic ¹ H NMR of the filtrate of 7-ClO ₄	S36
Figure S34: Paramagnetic ¹ H NMR of the precipitate of 7-ClO ₄	S37
Figure S35: ESI-MS of the filtrate and precipitate of 7-ClO ₄	S38
Figure S36: Paramagnetic ¹ H NMR of the precipitate of 7-Cl	
Figure S37: Paramagnetic ¹ H NMR of the filtrate of 7-Cl	S40
Figure S38: ESI-MS of the filtrate and precipitate of 7-CI	S41
Table S1: Summary of X-ray data collection and refinement for 1-3 and 8	S42
Table S2: Selected bond distances (Å) and angles (deg) for 1-3	S43
Table S3: Selected bond distances (Å) and angles (deg) for 8	S44
Figure S39-42: Paramagnetic ¹ H NMR of 1 under varying conditions over time	S45-S48
Figure S43-46: Paramagnetic ¹ H NMR of 2 under varying conditions over time	

Figure S47-50: Paramagnetic ¹ H NMR of 3 under varying conditions over timeS53-S56
Figure S51-55: Paramagnetic ¹ H NMR of 5 under varying conditions over timeS57-S61
Figure S56-60: Paramagnetic ¹ H NMR of 6 under varying conditions over timeS62-S66
Figure S61: Paramagnetic ¹ H NMR of 4 in CD ₃ CN with 5 equivalents of 10% D ₂ O (v:v) over timeS67
Figure S62: Paramagnetic ¹ H NMR of 8 in CD ₃ CN with 5 equivalents of 10% D ₂ O (v:v) over timeS68
Figure S63: UV-Vis spectrum comparison of 1 and 4 in CH ₃ CN over timeS69
Figure S64: UV-Vis spectrum comparison of 5 and 8 in CH ₃ CN over timeS70
Figure S65: ¹ H NMR of 1 dissolved in CH ₃ CN only with 1 equivalent of TERPYS71
Figure S66: ¹ H NMR of 5 dissolved in CH ₃ CN only with 1 equivalent of MBBPS72
Figure S67: ¹ H NMR of the organic recovery of complex 3S73
Figure S68: ¹ H NMR of the organic recovery of complex 7-ClO ₄
Figure S69: ¹ H NMR of the organic recovery of complex 3 under previous published condition
Figure S70: ESI-MS of the Organic recovery of complex 3 under previous published condition
Figure S71: ¹ H NMR of the organic recovery of complex 7-ClO₄ under previous published conditionsS77
Figure S72: ESI-MS of the Organic recovery of complex 7-CIO ₄ under previous published conditionsS78
Figure S73: ¹ H NMR of the organic recovery of complex 7-Cl under previous published conditionsS79
Figure S74: ESI-MS of the Organic recovery of complex 7-Cl under previous published conditionsS80



Figure S1: ¹H-NMR of **1** in CD₃CN (L= CH₃CN).



Figure S2: ¹H-NMR of **2** in CD₃CN (L= H_2O).



Figure S3: ¹H-NMR of **3** in CD₃CN (L= H_2O).



Figure S4: ¹H-NMR of **4** in CD_3CN .



Figure S5: ¹H-NMR of filtrate (top) and precipitate (bottom) from the reaction mixture of **1** in CD_3CN .



Figure S6: ¹H-NMR of filtrate (top) and precipitate (bottom) from the reaction mixture of **2** in CD_3CN .



Figure S7: ¹H-NMR of filtrate (top) and precipitate (bottom) from the reaction mixture of **3** in CD_3CN .



Figure S8: ESI-MS of 1 in CH₃CN.



Figure S9: ESI-MS of 2 in CH₃CN.



Figure S10: ESI-MS of 3 in CH₃CN.



Figure S11: ESI-MS of 4 in CH₃CN.



Figure S12: UV-Vis spectrum of 1 in CH_3CN (9.20x10⁻⁵ M)



Figure S13: UV-Vis spectrum of 2 in CH_3CN (7.24x10⁻⁵ M)



Figure S14: UV-Vis spectrum of 3 in CH_3CN (6.79x10⁻⁵ M)



Figure S15: UV-Vis spectrum of 4 in CH_3CN (3.85x10⁻⁵ M)



Figure S16: IR spectrum of 1



Figure S17: IR spectrum of 2



Figure S18: IR spectrum of 3



Figure S19: IR spectrum of 4



Figure S20: ¹H-NMR of **5** in CD₃CN (L= H_2O or CH₃CN). The hydrogen labelled "d" could not be labelled because the peak could not be found



Figure S21: ¹H-NMR of the filtrate (top) and a zoomed in diamagnetic region (bottom) from the reaction mixture of **5** in CD₃CN. The hydrogens labelled "d" and "g" could not be labelled because the peak could not be found (d) or due to overlap (g).



Figure S22: ¹H-NMR of **6** in CD₃CN (L= H_2O or CH₃CN). The hydrogens labelled "d" could not be labelled because the peak could not be found



Figure S23: ¹H-NMR of the filtrate (top) and a zoomed in diamagnetic region (bottom) from the reaction mixture of **6** in CD₃CN. The hydrogens labelled "d" and "e" could not be labelled because the peak could not be found (d) or due to overlap (e).



Figure S24: ESI-MS of the filtrate (top) and precipitate (bottom) from the reaction mixture of **5** in CH_3CN .



Figure S25: ESI-MS of the filtrate (top) and precipitate (bottom) from the reaction mixture of **6** in CH_3CN .



Figure S26: ¹H-NMR of **8** in CD₃CN.



Figure S27: ¹H-NMR of 8 in DMSO-d₆.



Figure S28: ESI-MS of 8 in CH₃CN.



Figure S29: UV-Vis spectrum of 8 in CH₃CN (5.35x10⁻⁵ M)



Figure S30: IR spectrum of 8



Figure S31: ¹H-NMR of the precipitate (top) and a zoomed in diamagnetic region (bottom) isolated during the attempted synthesis of **6** following previously published procedures (i.e. in glovebox with degassed solvents). The hydrogens labelled "d" could not be labelled because the peak could not be found.



Figure S32: ESI-MS of the isolated precipitate found during synthesis of **6** following previously published procedures (i.e. in glovebox with degassed solvents) in CH₃CN.



Figure S33: ¹H-NMR of the filtrate from the reaction mixture of **7-ClO**₄ in CD₃CN. Neither **7-ClO**₄ or **8** were observed.


Figure S34: ¹H-NMR of the precipitate of **7-ClO**₄ in CD₃CN (Top, L= H_2O or CH₃CN) and a zoomed in figure of the diamagnetic region (bottom). The hydrogens labelled "d" and "e" could not be labelled because the peak could not be found (d) or due to overlap (e).



Figure S35: ESI-MS of the filtrate (top) and precipitate (bottom) from the reaction mixture of **7-CIO**₄ in CH₃CN.



Figure S36: ¹H-NMR of the precipitate of **7-Cl** in DMSO (Top, $L = H_2O$ or DMSO) and a zoomed in figure of the diamagnetic region (bottom). This was taken after attempting to separate through a filter a second time. The hydrogens labelled "d" and "e" could not be labelled because the peak could not be found (d) or due to overlap (e).



Figure S37: ¹H-NMR of the filtrate of **7-Cl** in DMSO (Top, L= H_2O or DMSO) and a zoomed in figure of the diamagnetic region (bottom). This was taken after attempting to separate through a filter a second time. The hydrogens labelled "d" and "e" could not be labelled because the peak could not be found (d) or due to overlap (e). Magnified by 375x (relative to intensity of DMSO peak).

Figure S38: ESI-MS of the filtrate (top) and precipitate (bottom) from the reaction mixture of **7-CI** in CH_3CN .

	1	2	3	8
empirical formula	C22H21ClNiN4O6	C ₂₆ H ₃₂ ClNiN ₃ O ₄	C ₃₀ H ₂₄ ClNiN ₃ O ₇	C45H38.5Cl2N11.5NiO8
formula weight	531.59	592.70	632.68	997.98
crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
space group	C 1 2/c 1	P -1	P 1 21/c 1	P 1
<i>a</i> (Å)	15.6762(12)	9.9556(2)	18.6814(19)	12.2882(13)
<i>b</i> (Å)	13.2879(9)	11.6346(4)	10.5353(9)	19.219(2)
<i>c</i> (Å)	21.9128(18)	14.2457(4)	14.8709(14)	19.786(2)
α (deg)	90	110.337(3)	90	87.747(3)
β (deg)	91.405(3)	91.439(2)	109.241(3)	77.340(3)
γ (deg)	90	113.304(3)	90	77.490(3)
$V(Å^3)$	4563.1(6)	1395.42(8)	2763.3(5)	4450.7(8)
Ζ	8	2	4	4
density (calcd), Mg m ⁻³	1.548	1.411	1.521	1.489
temp (K)	100(1)	102(3)	100	105
crystal size (mm ³)	0.12 x 0.2 x 0.4	0.37 x 0.23 x 0.18	0.02 x 0.09 x 0.38	0.2 x 0.18 x 0.15
diffractometer	Bruker D8 Venture	Rigaku	Bruker D8 Venture	Bruker D8 Venture
Abs. coeff. (mm ⁻¹)	1.015	0.839	0.983	0.622
$2\theta \max(\deg)$	62.78	60.72	50.02	49.98
Reflections collected	9996	10275	9888	9194
Indep. reflections	7634	8096	4911	31034
variable parameters	310	355	387	2487
$R1 / wR2^b$	0.0319/0.0722	0.0329/.0774	0.0693/0.1995	0.0371/0.0769
goodness-of-fit (F^2)	1.031	1.053	1.191	1.029
largest diff. (e Å ⁻³)	0.519/-0.508	0.413/-0.536	1.56/-0.99	0.651/-0.431

Table S1. Summary of X-ray data collection and refinement for 1-3 and 8

^aRadiation used: Mo K α ($\lambda = 0.71073$ Å). ^bR1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$; wR2 = $[\sum [w(F_o^2 - F_c^2)^2] / [\sum (F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$.

	1	2	3	
Ni(1)-O(1)	2.0477(9)	2.0023(10)	1.982(4)	
Ni(1)-O(2)	1.9947(10)	1.9772(10)	2.018(4)	
Ni(1)-O(7)	-	2.1416(11)	2.094(4)	
Ni(1)-N(1)	2.0004(11)	1.9982(12)	1.997(5)	
Ni(1)-N(2)	2.1078(11)	2.0966(12)	2.107(5)	
Ni(1)-N(3)	2.1035(12)	2.1012(12)	2.135(5)	
Ni(1)-N(4)	2.4945(17)	-	-	
O(1)-C(16)	1.2707(16)	1.2626(17)	1.264(7)	
O(2)-C(19)	1.2688(16)	-	-	
O(2)-C(22)	-	1.2752(16)	-	
O(2)-C(24)	-	-	1.268(7)	
Ni(1)-O(7)	-	2.1416(11)	2.094(4)	
O(2)- Ni(1)-O(1)	90.59(4)	91.33(4)	89.96(16)	
O(2)- Ni(1)-N(1)	178.16(4)	176.30(5)	94.95(17)	
O(2)- Ni(1)-N(2)	100.46(4)	105.13(5)	94.55(18)	
O(2)- Ni(1)-N(3)	103.46(4)	98.43(5)	88.39(18)	
O(2)- Ni(1)-N(4)	86.89(4)	-	-	
O(2)- Ni(1)-O(7)		85.19(4)	171.59(16)	
O(1)- Ni(1)-N(1)	88.92(4)	90.31(4)	173.43(18)	
O(1)- Ni(1)-N(2)	94.41(4)	90.88(5)	96.52(18)	
O(1)- Ni(1)-N(3)	89.46(4)	91.52(5)	106.90(18)	
O(1)- Ni(1)-N(4)	176.56(4)	-	-	
O(1)- Ni(1)-O(7)	-	174.93(4)	83.14(17)	
N(1)- Ni(1)-N(2)	77.81(4)	78.16(5)	78.76(18)	
N(1)- Ni(1)-N(3)	78.31(4)	78.21(5)	77.67(18)	
N(1)- Ni(1)-N(4)	93.68(4)	-	-	
N(3)- Ni(1)-N(2)	155.72(4)	156.26(5)	156.41(18)	
N(4)- Ni(1)-N(2)	88.36(4)	97.37(15)	-	
N(4)- Ni(1)-N(3)	88.85(4)	-	-	
N(1)- Ni(1)-O(7)	-	93.38(4)	92.31(18)	
N(2)- Ni(1)-O(7)	-	86.49(4)	91.01(17)	
N(3)- Ni(1)-O(7)		92.63(5)	89.02(18)	

Table S2. Selected bond Distances (Å) and angles (deg) for 1-3

	8	
Ni(1B)-N(1B)	2.027(4)	
Ni(1B)-N(2B)	2.114(4)	
Ni(1B)-N(4B)	2.106(4)	
Ni(1B)-N(6B)	2.025(4)	
Ni(1B)-N(7B)	2.082(4)	
Ni(1B)-N(8B)	2.094(4)	
N(1B)-Ni(1B)-N(2B)	78.28(15)	
N(1B)-Ni(1B)-N(4B)	77.73(15)	
N(1B)-Ni(1B)-N(7B)	99.95(15)	
N(1B)-Ni(1B)-N(6B)	174.90(16)	
N(1B)-Ni(1B)-N(8B)	104.84(15)	
N(2B)-Ni(1B)-N(4B)	155.74(15)	
N(2B)-Ni(1B)-N(6B)	97.21(15)	
N(2B)-Ni(1B)-N(7B)	94.31(15)	
N(2B)-Ni(1B)-N(8B)	92.58(14)	
N(4B)-Ni(1B)-N(6B)	106.91(15)	
N(4B)-Ni(1B)-N(7B)	93.30(15)	
N(4B)-Ni(1B)-N(8B)	90.10(15)	
N(6B)-Ni(1B)-N(7B)	77.89(15)	
N(6B)-Ni(1B)-N(8B)	77.56(15)	
N(7B)-Ni(1B)-N(8B)	155.14(15)	

Table S3. Selected bond Distances (Å) and angles (deg) for $\mathbf{8}$

Figure S39: ¹H-NMR under paramagnetic conditions for **1** over time in dry CD₃CN only.

Figure S40: ¹H-NMR under paramagnetic conditions for **1** over time in dry CD_3CN with 5 equivalents of NEt₃.

Figure S41: ¹H-NMR under paramagnetic conditions for **1** over time in dry CD₃CN with 10% D₂O (v:v).

Figure S42: ¹H-NMR under paramagnetic conditions for **1** over time in dry CD₃CN with 5 equivalents of NEt₃ and 10% D₂O (v:v).

Figure S43: ¹H-NMR under paramagnetic conditions for **2** over time in dry CD₃CN only.

Figure S44: ¹H-NMR under paramagnetic conditions for **2** over time in dry CD_3CN with 5 equivalents of NEt₃.

Figure S45: ¹H-NMR under paramagnetic conditions for **2** over time in dry CD_3CN with 10% D_2O (v:v).

Figure S46: ¹H-NMR under paramagnetic conditions for **2** over time in dry CD₃CN with 5 equivalents of NEt₃ and 10% D_2O (v:v).

Figure S47: ¹H-NMR under paramagnetic conditions for **3** over time in dry CD₃CN only.

Figure S48: ¹H-NMR under paramagnetic conditions for **3** over time in dry CD_3CN with 5 equivalents of NEt₃.

Figure S49: ¹H-NMR under paramagnetic conditions for **3** over time in dry CD_3CN with 10% D_2O (v:v).

Figure S50: ¹H-NMR under paramagnetic conditions for **3** over time in dry CD₃CN with 5 equivalents of NEt₃ and 10% D_2O (v:v).

Figure S51: ¹H-NMR under paramagnetic conditions for **5** over time in dry CD₃CN only.

Figure S52: ¹H-NMR under paramagnetic conditions for **5** over time in dry CD_3CN with 5 equivalents of NEt₃.

Figure S53: ¹H-NMR under paramagnetic conditions for **5** over time in dry CD_3CN with 10% D_2O (v:v).

Figure S54: ¹H-NMR under paramagnetic conditions for **5** over time in dry CD₃CN with 5 equivalents of NEt₃ and 10% D_2O (v:v).

Figure S55: ¹H-NMR under paramagnetic conditions for **5** over time in dry CD_3CN with 1 equivalent of NEt_3 .

Figure S56: ¹H-NMR under paramagnetic conditions for **6** over time in dry CD₃CN only.

Figure S57: ¹H-NMR under paramagnetic conditions for **6** over time in dry CD₃CN with 5 equivalents of NEt₃.

Figure S58: ¹H-NMR under paramagnetic conditions for **6** over time in dry CD_3CN with 10% D_2O (v:v).

Figure S59: ¹H-NMR under paramagnetic conditions for **6** over time in dry CD₃CN with 5 equivalents of NEt₃ and 10% D_2O (v:v).

Figure S60: ¹H-NMR under paramagnetic conditions for 6 over time in dry CD₃CN with 1 equivalent of NEt₃.

Figure S61: ¹H-NMR under paramagnetic conditions for **4** at the start and 24 hours later in dry CD_3CN with 5 equivalents of NEt₃ and 10% D_2O (v:v).

Figure S62: ¹H-NMR under paramagnetic conditions for **8** at the start and 24 hours later in dry CD₃CN with 5 equivalents of NEt₃ and 10% D_2O (v:v).

Figure S63: UV-Vis absorption spectra of **1** (top) and **4** (bottom) over time. Concentration: 5.00×10^{-4} M. Conditions: CH₃CN, 10% D₂O (v:v), 5 eq NEt₃, RT.

Figure S64: UV-Vis absorption spectra of **5** (top) and **8** (bottom) over time. Concentration: 5.00×10^{-4} M. Conditions: CH₃CN, 10% D₂O (v:v), 5 eq NEt₃, RT.

Figure S65: ¹H-NMR under paramagnetic conditions for **1** over time in dry CD₃CN only with 1 equivalent of TERPY.

Figure S66: ¹H-NMR under paramagnetic conditions for **5** over time in dry CD₃CN only with 1 equivalent of MBBP.


Figure S67: Organic recovery of a reaction mixture of **3** after 24 hours in CH₃CN, 10% H₂O (v:v) and 100 equivalents of NEt₃ with O₂ (Solvent: CDCl₃).



Figure S68: Organic recovery of a reaction mixture of **7** after 24 hours in CH_3CN , 10% H_2O (v:v) and 100 equivalents of NEt₃ with O_2 (Solvent: $CDCl_3$). The reagents of **7** were mixed together first for 30 minutes prior to addition of the other reagents.



Figure S69: Organic recovery of a reaction mixture of **3** after 24 hours in dry CH_3CN and 1 equivalent of NEt₃ with O_2 (Solvent: CDCl₃).



Figure S70: ESI-MS of a reaction mixture of **3** before O_2 purge (top) and O_2 purge and a 24 hour stir period (bottom) in dry CH₃CN and 1 equivalent of NEt₃.



Figure S71: Organic recovery of a reaction mixture of **7-ClO**₄ after 24 hours in dry CH₃CN and 1 equivalent of NEt₃ with O₂ (Solvent: CDCl₃). The reagents of **7-ClO**₄ were mixed together first for 30 minutes prior to addition of the other reagents.



Figure S72: ESI-MS of a reaction mixture of **7-ClO**₄ before O_2 purge (top) and O_2 purge and a 24 hour stir period (bottom) in dry CH₃CN and 1 equivalent of NEt₃.



Figure S73: Organic recovery of a reaction mixture of **7-Cl** after 24 hours in dry CH_3CN and 1 equivalent of NEt₃ with O₂ (Solvent: CDCl₃). The reagents of **7-Cl** were mixed together first for 30 minutes prior to addition of the other reagents.



Figure S74: ESI-MS of a reaction mixture of **7-CI** before O_2 purge (top) and O_2 purge and a 24 hour stir period (bottom) in dry CH₃CN and 1 equivalent of NEt₃.