Supporting Information for:

Divergent Solution and Solid State Structures of Mono- and Di-Nuclear Nickel(II) Pyridone Complexes

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Crystallographic Data Collection and Structure Solution

Crystallization conditions for all compounds were described above in the Synthetic Procedures section. The data for compounds **2**, **4** and **6** were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focus Cu Kα radiation source (λ = 1.5418 Å) with collimating mirror monochromators. The data were collected at 100 K using an Oxford Cryostream low temperature device. The data for compounds **1**, **3** and **5** were collected on a Rigaku AFC12 diffractometer with a Saturn 724+ CCD using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å).

Details of crystal data, data collection and structure refinement are listed below in **Tables S1-S6**. Data collection, unit cell refinement and data reduction were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.40.53.[1] The structure was solved by direct methods using SHELXT[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3.[3] Structure analysis was aided by use of the programs PLATON[4], OLEX2[5] and WinGX.[6] The hydrogen atoms on the carbon atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 × U_{eq} of the attached atom (1.5 × U_{eq} for methyl hydrogen atoms).

The function, $\Sigma w(|F_O|^2 - |F_C|^2)^2$, was minimized (See **Tables S1-S6** for weights and refinement parameters). Definitions used for calculating R(F), R*w* (F^2) and the goodness of fit, S, are given below.[7] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[8] All figures were generated using SHELXTL/PC.[9]

Table S1. Crystallographic Data and Refinement Parameters for **1**, *NNS* ligand

Empirical formula	$C_{14}N_2OS$	
Formula weight	258.33 g/mol	
Temperature	150.0 K	
Wavelength	0.71075 Å (Mo Kα)	
Crystal system	monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 11.990(3) Å b = 6.6546(19) Å c = 16.284(5) Å	α = 90° β = 94.939(7)° γ = 90°
Volume	1294.5(6) Å^3	
Z	4	
Density	1.326 g/cm^3	
Absorption coefficient	0.239 mm^{-1}	
F(000)	544	
Crystal size	0. 113 x 0.089 x 0.063 mm	
Theta rage for data collection	$-15 \leq h \leq 15$ $-8 \leq k \leq 8$ $-21 \leq l \leq 21$	
Completeness	95.88%	
Weight	$w = 1/[\Sigma^2(F_0^2 + (0.0227P)^2 + 3.2296P]$ where $p = (F_0^2 + 2\,F_c^2)/3$	
Goodness-of-fit on F^2	1.005	
Final R indicies [I > 2sigma(I)]	R_1 = 0.0585 wR_2 = 0.1026	
R indicies (all data)	R_1 = 0.0893 wR_2 = 0.1154	

Table S2. Crystallographic Data and Refinement Parameters for **2**, $[Ni_2(NNS)_4(F)][BF_4]$

Empirical formula	$C_{57}H_{58}BF_5N_8Ni_2O_6S_4$	
Formula weight	1354.48 g/mol	
Temperature	100.(2) K	
Wavelength	1.54184 Å (Cu Kα)	
Crystal system	monoclinic	
Space group	P121/c1	
Unit cell dimensions	a = 16.4278(4) Å b = 16.0410(3) Å c = 22.8488(4) Å	α = 90° β = 91.4804(19)° γ = 90°
Volume	6019.1(2) Å^3	
Z	4	
Density	1.495 g/cm^3	
Absorption coefficient	3.475 mm^{-1}	
F(000)	2796	
Crystal size	0.111 x 0.102 x 0.081 mm	
Theta rage for data collection	$-18 \leq h \leq 20$ $-19 \leq k \leq 19$ $-28 \leq l \leq 24$	
Completeness	98.31%	
Weight	$w = 1/[\Sigma^2(F_0^2 + (0.1264P)^2]$ where $p = (F_0^2 + 2\,F_c^2)/3$	
Goodness-of-fit on F^2	1.090	
Final R indicies [I > 2sigma(I)]	R_1 = 0.0842 wR_2 = 0.2028	
R indicies (all data)	R_1 = 0.1194 wR_2 = 0.2352	

Table S3. Crystallographic Data and Refinement Parameters for **3**, $[Ni_2(NNS)_4(Cl)]$

Empirical formula	$C_{36}H_{24}Cl_{0.25}N_2Ni_2O_4S_2$	
Formula weight	738.97 g/mol	
Temperature	100.(2) K	
Wavelength	0.71073 Å (Mo Kα)	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.1838(6) Å b = 15.2354(5) Å c = 15.4852(6) Å	α = 93.934(3)° β = 114.696(4)° γ = 105.200(3)°
Volume	3075.2(2) Å^3	
Z	4	
Density	1.596 g/cm^3	
Absorption coefficient	1.427 mm^{-1}	
F(000)	1513	
Crystal size	0.102 x 0.092 x 0.087 mm	
Theta rage for data collection	$-18 \leq h \leq 18$ $-18 \leq k \leq 18$ $-16 \leq l \leq 18$	
Completeness	99.69	
Weight	$w = 1/[\Sigma^2(F_0^2 + (0.0711P)^2 + 26.7207P]$ where $p = (F_0^2 + 2\,F_c^2)/3$	
Goodness-of-fit on F^2	1.090	
Final R indices [I > 2sigma(I)]	R_1 = 0.0862 wR_2 = 0.1979	
R indices (all data)	R_1 = 0.1037 wR_2 = 0.2066	

Table S4. Crystallographic Data and Refinement Parameters for **4**, $Ni_2(NNS)_3(OAc)_2(OH_2)$

Empirical formula	$C_{46}H_{48}N_6Ni_2O_8S_3$	
Formula weight	1026.50 g/mol	
Temperature	99.97(13) K	
Wavelength	1.54184 Å (Cu Kα)	
Crystal system	trigonal	
Space group	P-3	
Unit cell dimensions	a = 26.0235(5) Å b = 26.0235(5) Å c = 14.9254(4) Å	α = 90° β = 90° γ = 120°
Volume	8753.6(4) Å^3	
Z	6	
Density	1.168 g/cm^3	
Absorption coefficient	2.198 mm^{-1}	
F(000)	3204	
Crystal size	0.120 x 0.097 x 0.092 mm	
Theta rage for data collection	$-31 \leq h \leq 15$ $-13 \leq k \leq 24$ $-16 \leq l \leq 17$	
Completeness to theta	96.81%	
Weight	$w = 1/[\Sigma^2(F_0^2 + (0.1776P)^2 + 4.6492P]$ where $p = (F_0^2 + 2\,F_c^2)/3$	
Goodness-of-fit on F^2	1.237	
Final R indices [I > 2sigma(I)]	R_1 = 0.0892 wR_2 = 0.2281	
R indices (all data)	R_1 = 0.1156 wR_2 = 0.2532	

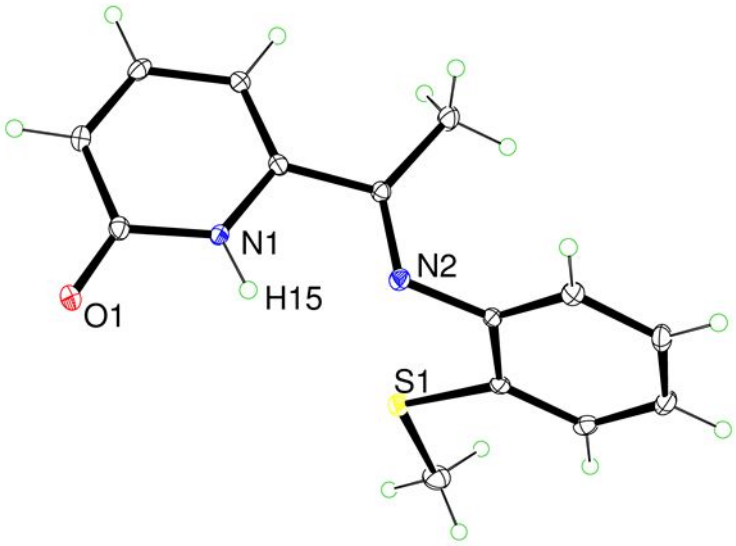
Table S5. Crystallographic Data and Refinement Parameters for **5**, Ni(*NNS*)$_2$(MeOH)$_2$

Empirical formula	$C_{30.25}H_{36}N_4NiO_{5.75}S_2$	
Formula weight	670.46 g/mol	
Temperature	100.(2) K	
Wavelength	0.71073 Å (Mo Kα)	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.3252(16) Å b = 12.293(2) Å c = 14.310(2) Å	α = 104.234(4)° β = 90.349(4)° γ = 90.154(4)°
Volume	1589.9(5) Å^3	
Z	2	
Density	1.400 g/cm^3	
Absorption coefficient	0.789 mm^{-1}	
F(000)	703	
Crystal size	0.112 x 0.095 x 0.089 mm	
Theta rage for data collection	$-12 \leq h \leq 12$ $-15 \leq k \leq 15$ $-18 \leq l \leq 18$	
Completeness	100.00%	
Weight	$w = 1/[\Sigma^2(F_0^2 + (0.0539P)^2 + 1.9929P]$ where $p = (F_0^2 + 2 F_c^2)/3$	
Goodness-of-fit on F^2	1.030	
Final R indices [I > 2sigma(I)]	R_1 = 0.0458 wR_2 = 0.1125	
R indices (all data)	R_1 = 0.0575 wR_2 = 0.1196	

Table S6. Crystallographic Data and Refinement Parameters for **6**, Ni(*NNS*)$_2$(OAc)(OH$_2$)

Empirical formula	$C_{32}H_{36}N_5NiO_6S_2$	
Formula weight	709.49 g/mol	
Temperature	99.9(3) K	
Wavelength	1.54184 Å (Cu Kα)	
Crystal system	orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 15.2902(8) Å b = 27.9244(16) Å c = 15.7755(6) Å	α = 90° β = 90° γ = 90°
Volume	6735.7(6) Å^3	
Z	8	
Density	1.399 g/cm^3	
Absorption coefficient	2.410 mm^{-1}	
F(000)	2968	
Crystal size	0.167 x 0.140 x 0.036 mm	
Theta rage for data collection	-18 ≤ h ≤ 13 -34 ≤ k ≤ 34 -19 ≤ l ≤ 13	
Completeness	98.53%	
Weight	w = 1/[Σ^2(F_0^2 + (0.0557P)^2 + 123.2411P] where p = (F_0^2 + 2 F_c^2)/3	
Goodness-of-fit on F^2	1.187	
Final R indices [I > 2sigma(I)]	R_1 = 0.1570 wR_2 = 0.3288	
R indices (all data)	R_1 = 0.1740 wR_2 = 0.3380	

Figure S1. ORTEP diagram of **1** shown as 50% probability thermal ellipsoids.



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2) SHELXT. (2015). G. M. Sheldrick. A program for crystal structure solution. *Acta Cryst.* A71, 3-8.

3) Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. *Acta Cryst.* C71, 9-18.

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6) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. *J. Appl. Cryst.* 32. 837-838.

7) $R_W(F^2) = \{\Sigma w(|F_O|^2 - |F_C|^2)^2/\Sigma w(|F_O|)^4\}^{1/2}$ where w is the weight given each reflection.
$R(F) = \Sigma(|F_O| - |F_C|)/\Sigma|F_O|\}$ for reflections with $F_O > 4(\sigma(F_O))$.
$S = [\Sigma w(|F_O|^2 - |F_C|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

8) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press

9) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.