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Tetranuclear nickel(II) complex with tetra-coordinated acetate and 1,3,5-tris(2-hydroxyphenyl)-2,4-diazapenta-1,4-diene ligands

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Synthesis and characterization

The ^{1}H and ^{13}C NMR spectra of proligand **1** were recorded at 298 K on a Bruker Avance 300 spectrometer operating at 400 and 100 MHz, respectively. Chemical shifts were referenced to residual DMSO-d_6 (δ_H = 2.50 ppm) for ^{1}H and DMSO-d_6 (δ_C = 39.5 ppm) for ^{13}C. NMR data are reported as follows: chemical shift (δ, ppm), multiplicity, coupling constant (J, Hz), and integration.

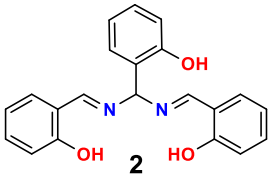
Single-crystal X-ray diffraction data for compound 3 were collected at 100 K using a Bruker D8 QUEST diffractometer equipped with a Photon III detector. The crystal structure was solved by dual-space methods using SHELXT and refined within the Olex2 software package.

All reagents and solvents were purified prior to use. Salicylaldehyde was freshly distilled under reduced pressure. Pyridine was distilled over potassium hydroxide and then redistilled over barium oxide. Ethanol was dried over calcium oxide and distilled over magnesium powder. Dichloromethane was dried over phosphorus pentoxide, and diethyl ether was distilled over sodium.

Anhydrous nickel acetate monoacetic acid ($Ni(OAc)_2 \cdot AcOH$)[S1]

Anhydrous nickel acetate monoacetic acid, $Ni(OAc)_2 \cdot AcOH$, was prepared from 15 g of $Ni(OAc)_2 \cdot 4H_2O$ by refluxing in 150 mL of acetic anhydride for 16 h. The resulting dark green crystals were collected by filtration, washed with acetic anhydride, and dried in a vacuum desiccator over NaOH, followed by additional drying at 70 °C under reduced pressure (0.1 Torr) for 5 h. Yield: 10.5 g (74%). Elemental analysis: found: C, 31.09%; H, 4.35%; Ni, 24.27%; calculated for $C_6H_{10}NiO_6$: C, 30.43%; H, 4.26%; Ni, 24.78%.

1,3,5-Tris(2-hydroxyphenyl)-2,4-diazapenta-1,4-diene (2)[S2]

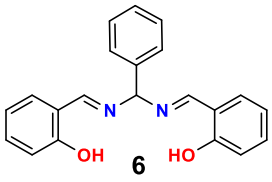


2

To a solution of salicylaldehyde (10.0 g, 81.9 mmol) was added 100 mL of 25% aqueous ammonia and ammonium chloride (1.0 g, 0.23 mol). The reaction mixture was stirred at room temperature for 24 h. The resulting yellow solid was filtered off to yield 7.6 g (80%) of compound **2**. Melting point: 164 °C (decomp.) (lit. 164 °C).

^{1}H NMR (400 MHz, DMSO-d_6) δ 13.17 (s, 3H, OH), 8.80 (s, 2H, CH=N), 7.55 (dd, J = 8.4, 1.7 Hz, 2H), 7.44 – 7.31 (m, 3H), 7.18 (td, J = 8.3, 1.8 Hz, 1H), 6.99 – 6.77 (m, 6H), 6.36 (s, 1H, N–CH–N) (Fig. S1, S2). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.2, 160.3, 154.7, 133.0, 132.2, 129.3, 127.4, 126.7, 119.3, 119.0, 118.7, 116.6, 115.8, 84.1 (Fig. S3). Elemental analysis calculated for $C_{21}H_{18}N_2O_3$ (%): C 72.82, H 5.24, N 8.09; found: C 72.14, H 5.25, N 8.09.

1,5-bis(2-hydroxyphenyl)-3-phenyl-2,4-diazapentadiene (6)[S3]

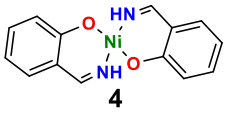


6

A mixture of 1.7 g (4.9 mmol) of 1,3,5-tris(2-hydroxyphenyl)-2,4-diazapentadiene, 1.0 g (9.4 mmol) of benzaldehyde, and 1.2 g (15.6 mmol) of ammonium acetate in 6 mL of methanol was stirred at room temperature for 2 days. The resulting yellow precipitate was filtered off, washed with methanol (3 × 5 mL), and dried. Yield: 1.5 g (96%). Melting point: 123–124 °C (lit. 123–124 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.94 (s, 2H, OH), 8.58 (s, 2H, CH=N), 7.49 – 7.29 (m, 9H), 6.99 (dd, *J* = 8.3, 1.1 Hz, 2H), 6.91 (td, *J* = 7.5, 1.1 Hz, 2H), 6.01 (s, 1H, N–CH–N) (Fig. S4, S5).

bis[2-(iminomethyl)phenolato-k^2N,O′]nickel(II) (4)



4

Complex 4 was obtained as a byproduct in the synthesis of compound **3** as dark red crystals.[S4] ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.60 (d, *J* = 11.7 Hz, 2H), 7.76 (d, *J* = 11.7 Hz, 2H), 7.32 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.13 (ddd, *J* = 8.7, 6.9, 1.8 Hz, 2H), 6.65 (d, *J* = 8.5 Hz, 2H), 6.50 (ddd, *J* = 7.9, 6.8, 1.1 Hz, 2H) (Fig. S6).

Ni(II) Complex (3)

From proligand **2**.

A mixture of $Ni(OAc)_2$·AcOH 0.6 g (2.6 mmol) and proligand **2** 1.8 g (5.2 mmol) was dissolved in 19 mL of anhydrous ethanol in presence or absence of 0.1 g (2.6 mmol) NH_4Cl. Freshly distilled pyridine (7 mL) was added, and the reaction mixture was stirred at room temperature for 20 minutes. A small amount of a red precipitate of Ni(II) salicyliminate formed immediately and was removed by filtration. The resulting clear green solution was evaporated to dryness, then redissolved in a solvent mixture of absolute EtOH:CH_2Cl_2:Et_2O (3:2:1) and stored at –3 to 0 °C for 4–7 days. Deep green crystalline material was obtained and collected by filtration. Yield 0.5 g (13%) without NH_4Cl or 2 g (56%) in presence of NH_4Cl. The crystallographic data for complex **3** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under Deposition Number 2429153.

From proligand **6**.

A mixture of $Ni(OAc)_2$·AcOH 0.6 g (2.6 mmol) and proligand **6** 1.7 g (5.2 mmol) was dissolved in 19 mL of anhydrous ethanol. Freshly distilled pyridine (7 mL) was added, and the reaction mixture was stirred at room temperature for 20 minutes. A small amount of a red precipitate of Ni(II) salicyliminate formed immediately and was removed by filtration. The resulting clear green solution was evaporated to dryness, then redissolved in a solvent mixture of absolute EtOH:CH_2Cl_2:Et_2O (3:2:1) and stored at –3 to 0 °C for 4–7 days. Deep green crystalline material was obtained and collected by filtration. Yield of complex **3** 0.5 g (13%). The single crystal X-ray data were identical to data of complex obtained from proligand **2**.

Calculations of crystal structures energies

Calculations of the energies of the crystal structures were carried out using the GPAW program[S5] based on the projector-augmented wave method and self-consistent density functional theory (DFT) equations using plane waves at the PBE (Perdew–Burke–Ernzerhof exchange-correlation functional) level of theory.[S6] All calculations are carried out at 0 K and 0 atm. The plane-wave kinetic energy cutoff was set to 520 eV. The geometries were considered converged when the net forces were all less than 0.03 eV/Å.

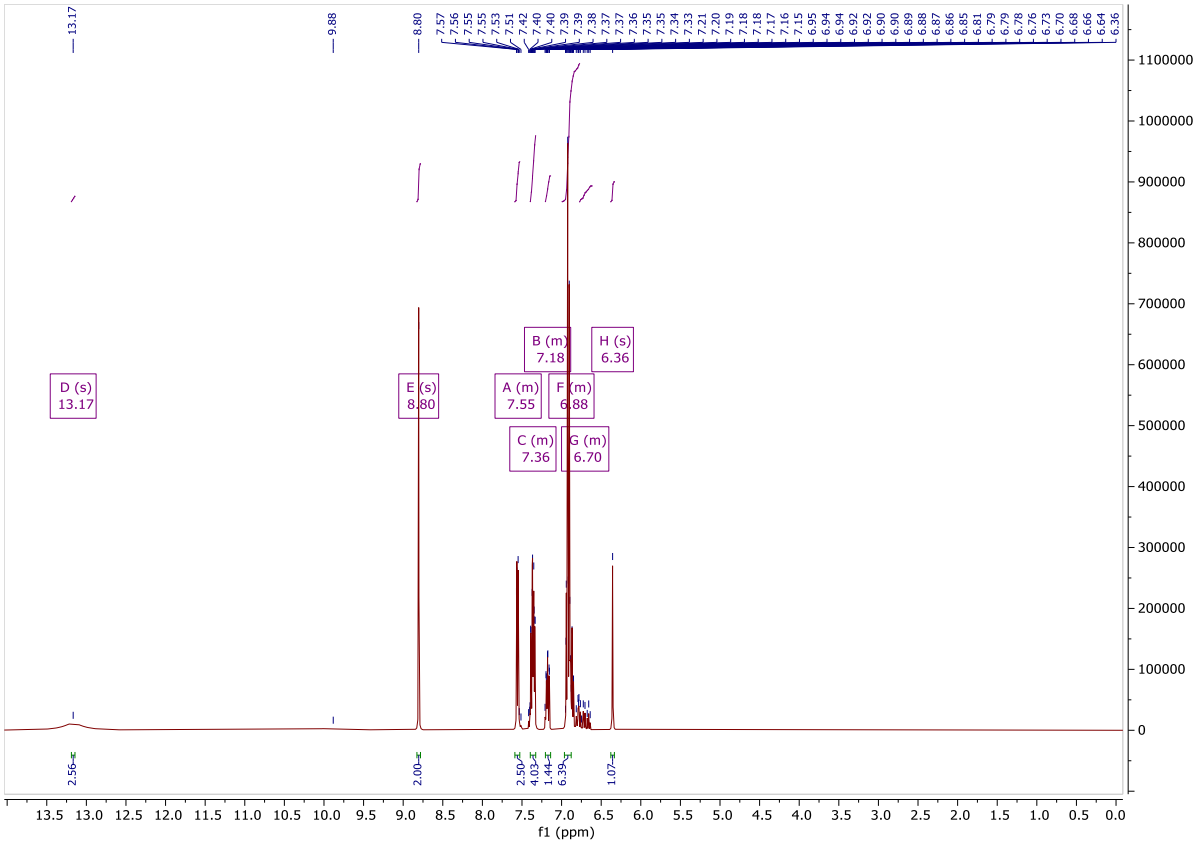


Figure S1. Full ^{1}H NMR data for compound **2**.

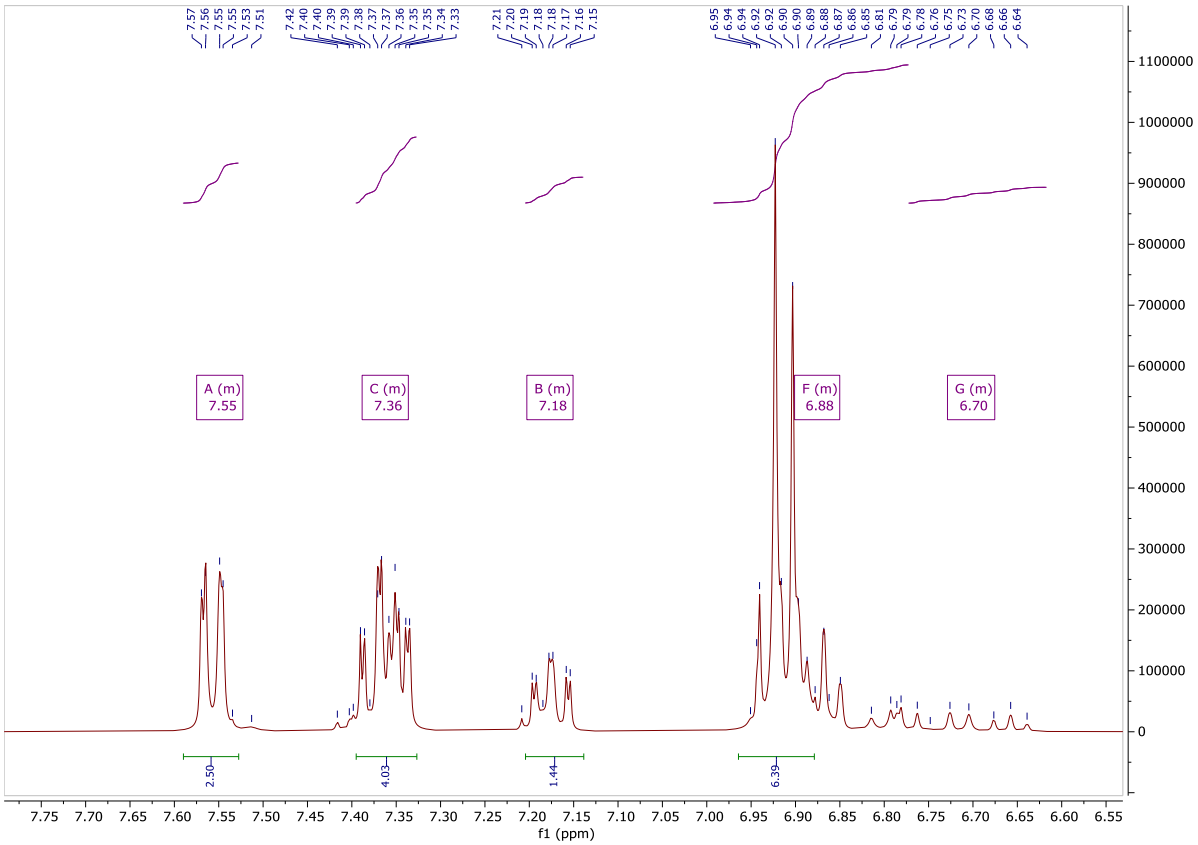


Figure S2. 6.5-7.7 ppm ^{1}H NMR data for compound **2**.

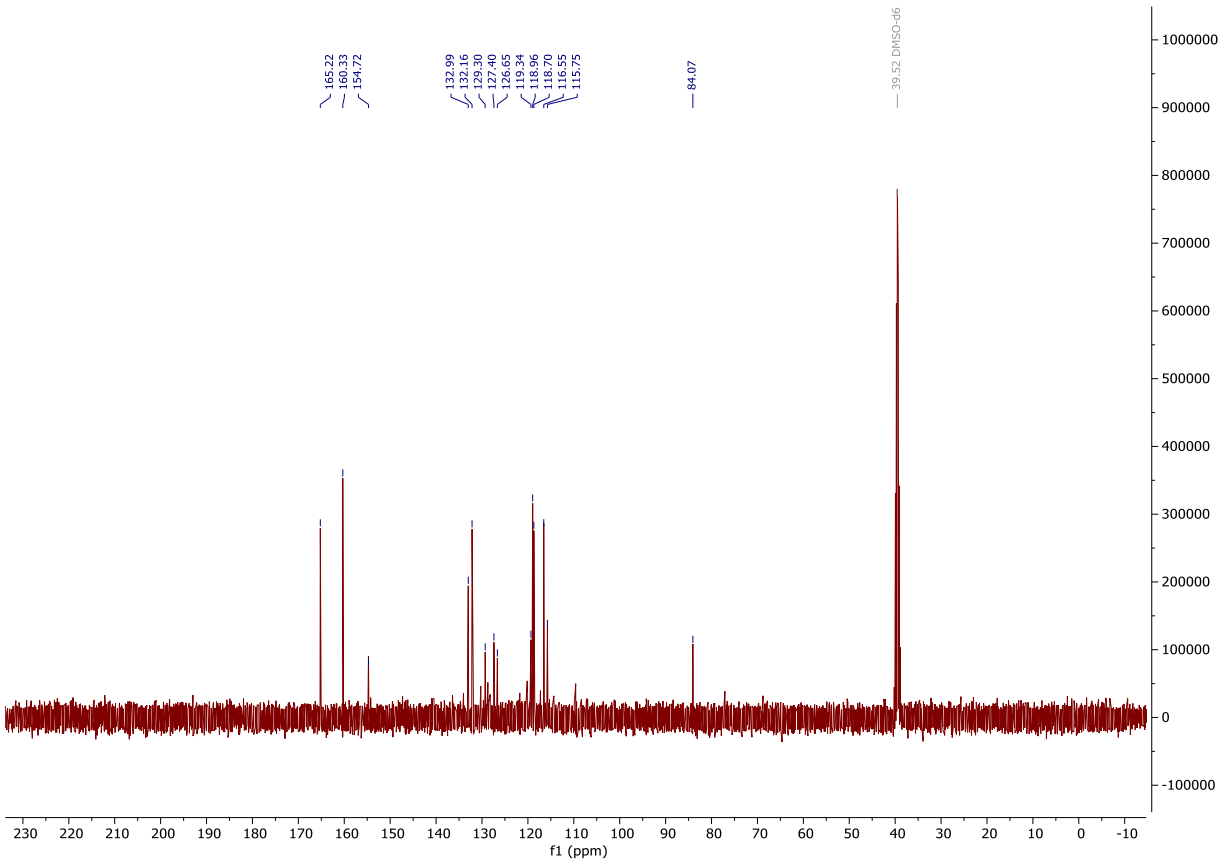


Figure S3. ^{13}C NMR data for compound **2**.

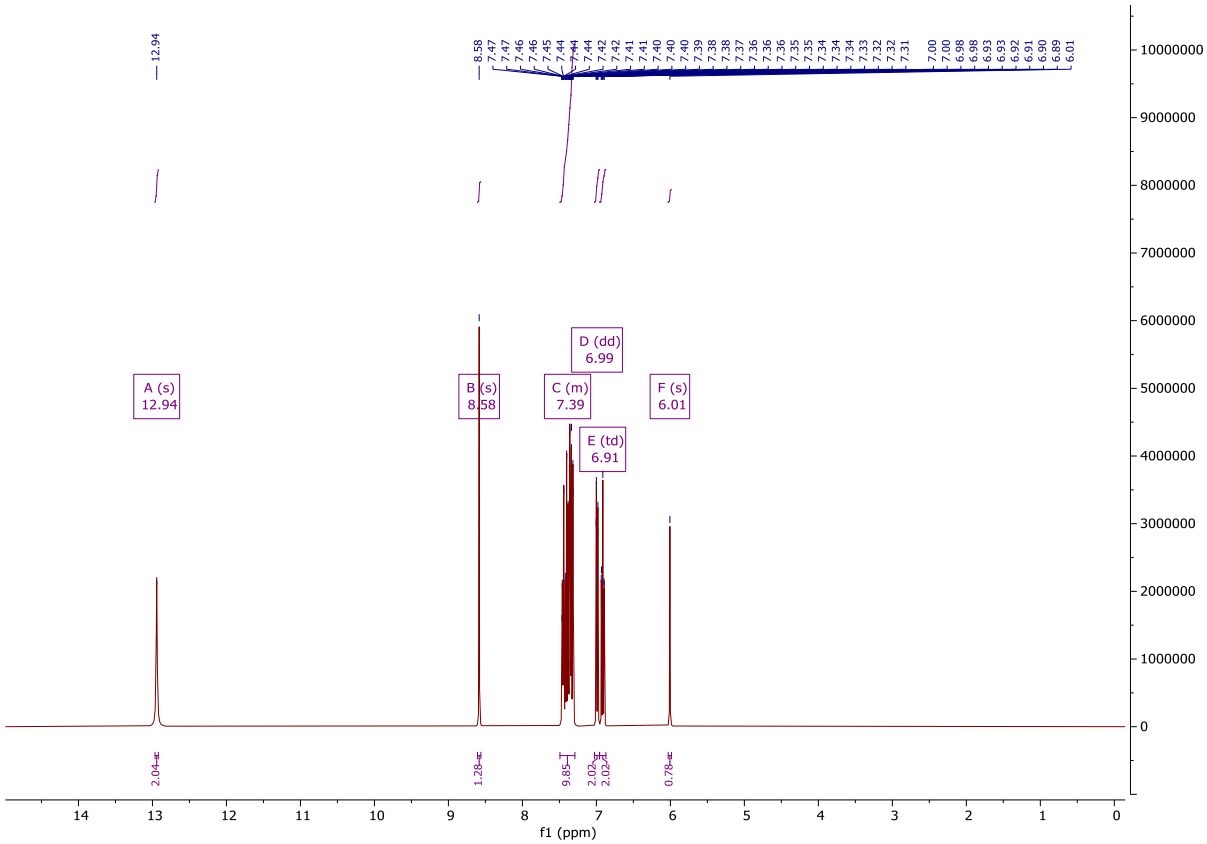


Figure S4. Full ^{1}H NMR data for compound **6**.

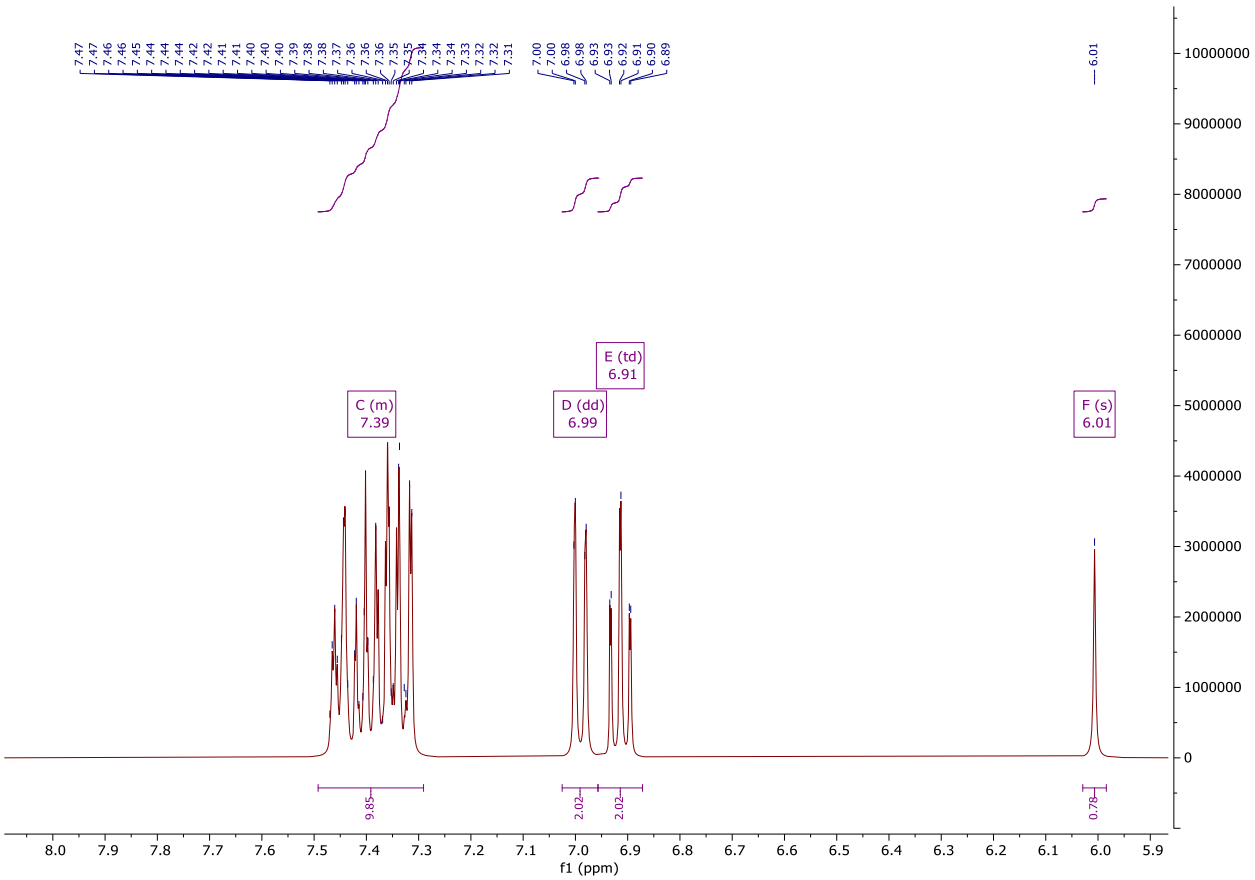


Figure S5. 6.0-8.0 ppm ^{1}H NMR data for compound **2**.

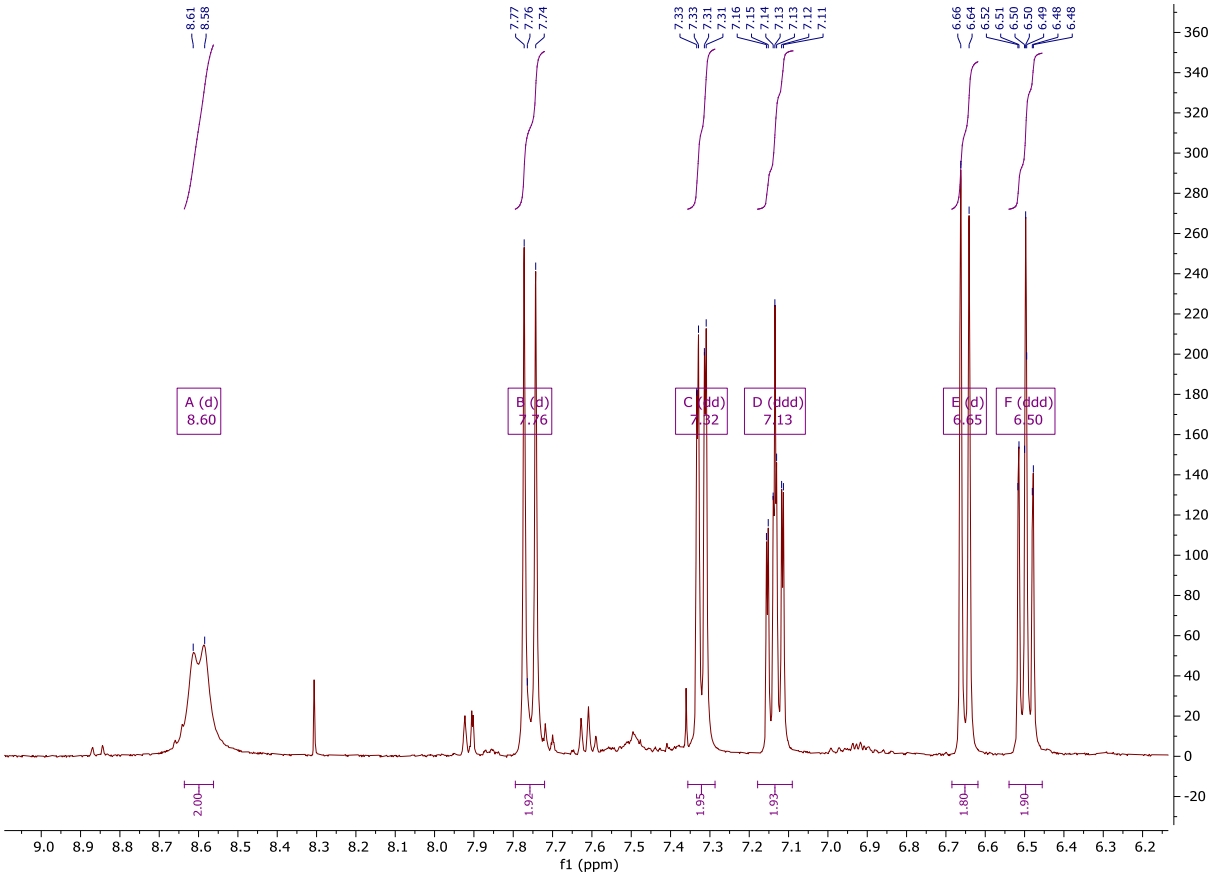


Figure S6. ^{1}H NMR data for complex **4**.

Table S1 Reagent Preparation and Crystal growth conditions for the Synthesis of Complexes **3** and **5**.

	Complex (**5**)	Complex (**3**)
Reaction conditions for proligand (**2**) synthesis	Salicylic aldehyde, $NH_{3(aq.)}$, room temperature, 24 h	Salicylic aldehyde, $NH_{3(aq.)}$, NH_4Cl (20 mol%), room temperature, 8 h
$Ni(OAc)_2*4H_2O$ drying	Heating of dry powder under reducing pressure (1 Torr) until hydrated water evaporated and greenish-blue crystals of $Ni(OAc)_2*2H_2O$ were obtained	Heating the salt solution in acetic anhydride with reflux for 8 h, deep green precipitate $Ni(OAc)_2*AcOH$ was obtained
Crystal growing	Crystals were grown from reaction mixture, pyridine/abs. ethanol (1:3 v/v)	Reaction mixture in pyridine/abs. ethanol (1:2.7 v/v) was evaporation to dry. Crystals were grown from abs. $EtOH:CH_2Cl_2:Et_2O$ (3:2:1 v/v)

Table S2 Selected characteristics of the newly obtained compound **3** and previously reported compound **5**.

Description	Complex (**3**)	Complex (**5**)
CCDC	2429153	2404114
Molecular formula of complex	$C_{66}H_{61}N_8Ni_4O_{10}$	$C_{62}H_{50}N_8Ni_3O_6$
Molecular formula of crystal cell	$C_{70}H_{72}ClN_8Ni_4O_{12}$	$C_{74}H_{66}N_{10}Ni_3O_7$
Space group	$P2_12_12_1$	P-1
Color	emerald green	emerald green
Number of nuclei (Ni)	4	3
Main proligand (quantity)	1,3,5-Tris(2-hydroxyphenyl)-2,4-diazapenta-1,3-diene (2)	1,3,5-Tris(2-hydroxyphenyl)-2,4-diazapenta-1,3-diene (2)
Auxiliary ligands (quantity)	Pyridine (4), Acetate (1), Ethanol (1), Water (1)	Pyridine (4)
Coordination geometry	octahedral	octahedral
Maximum deviation from geometry, °	76.92 (O3S-Ni1-O2)	79.95 (O5-Ni3-O3)
Calculated energies (DFT, LCAO, dzp basis), eV/atom	6.42	6.59
Range of distances (Ni-Ligand), A		
Ligand 1	2.009-2.060	2.038-2.075
Pyridine	2.093-2.129	2.109-2.118
Acetate	2.099-2.253	
Ethanol	2.123	
Water	2.091	

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