Strong ferromagnetic metal-ligand exchange in a nickel bis(3,5-dipyridylverdazyl) complex.

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Supporting Information: Experimental Details

tert-butyl 2-isopropyl-2-{[(2)-1-(pyridin-2-yl)-2-(pyridin-2-ylmethylidene)hydrazinyl]carbonyl}hydrazinecarboxylate (3)

Pyridine-2-carboxaldehyde-2'-pyridylhydrazone (papyH, 2.32 g, 12.5 mmol) was suspended in 60mL toluene and 3.5 mL (25 mmol) triethylamine. Triphosgene (1.24 g, 4.18 mmol) was added and the suspension stirred rapidly at room temperature under nitrogen. After 2.3 hours a solution of iPr-NHNH-Boc[1] (1.90 g, 11 mmol) dissolved in 20 mL toluene was added. After a further 2 hours vigorous stirrring, the precipitated triethylamine hydrochloride was removed by gravity filtration and rinsed with toluene. The organic solution was evaporated to give an orange oil which was dissolved in dichloromethane and purified by chromatography on a short silica gel column eluting with 60/40 EtOAc/CH_2Cl_2. The product oil with Rf=0.65 was crystallized by dissolution in hot heptane,cooling and chilling in a freezer for 5 days. Lemon-colored, powdery crystals of **3** (3.21 g, 66%) were isolated by vacuum filtration. m.p. 125-129˚C; δ_H (300 MHz, 55°C, $CDCl_3$) 8.57 (m, 1H), 8.20 (m, 1H), 8.12 (s, 1H), 7.94 (m, 1H), 7.67 (m, 3H), 7.51 (m, 1H), 7.18 (t, 1H, J=5.1), 6.94 (t, 1H, J=5.0), 6.70 (bs, 1H), 4.72 (septet, 1H, J=6.5), 1.30 (s, 9H), 1.26 (d, 6H, J=6.5). δ_C (300 MHz, 55°C, $CDCl_3$) 156.7, 156.0, 155.6, 154.4, 149.7, 148.0, 145.0, 138.7, 136.2, 123.5, 120.3, 118.4, 111.8, 81.9, 50.6, 28.2, 19.6;IR (film on NaCl plate) 3261 (NH), 3063, 2980, 2934, 1703 (C=O), 1591, 1568, 1467, 1433, 1397, 1369, 1312, 1246, 1158, 776, 735 cm^{-1}; MS (EI) m/z (relative intensity) 399 (M+1, 1) 341 (10), 281 (12) 200 (14) 144 (25), 127 (50) 102 (30), 85 (40), 57 (100)

1-isopropyl-3,5-di(2'-pyridyl)-6-oxotetrazane (4)

Compound **3** (2.64 g, 6.86 mmol) and concentrated HCl (5.7 mL) were combined in a 250 mL Erlenmeyer flask. Rapid dissolution with effervescence occurred, completing in approximately one minute. The mixture was neutralized with saturated $NaHCO_3$ (~100 mL), producing a yellow liquid with some yellow solid deposits on the glass. The reaction mixture was extracted with ~150 mL dichloromethane and the organic layer dried over magnesium sulfate filtered and evaporated to give a yellow syrup. This was crystallized by dissolution in minimal hot toluene, cooling in the freezer, and adding a little cold hexanes, which caused immediate precipitation. Filtration gave dusty yellow crystals of 1-isopropyl-3,5-di(2'-pyridyl)-6-oxotetrazane (1.26 g, 62%) with mp 119.6-122.8°C, ν_{max}(NaCl plate)/cm^{-1} 3257 (NH), 3054 (CH), 2974 (CH), 1644 (C=O); δ_H (300 MHz, $CDCl_3$) 8.59 (d, 1H, J=4.8), 8.39 (dd, 1H, J=4.8, 1.5), 7.84 (d, 1H, J=8.1), 7.75 (td, 1H, J=7.5, 2.1), 7.64 (td, 1H, J=7.2, 2.3), 7.49 (d, 1H, J=7.5), 7.32 (ddd, 1H, J=7.6, 5.0, 1.1), 7.00 (ddd, 1H, J=7.0, 5.0, 1.0), 6.01 (d, 1H, J=9.6), 5.01 (t, 1H, J=10.5), 4.75 (septet, 1H, J=6.8), 4.69 (d, 1H, J=11.7), 1.21 (d, 3H, J=6.8), 1.15 (d, 3H, J=6.8); δ_C (300 MHz, $CDCl_3$) 153.9, 153.6, 152.3, 149.4, 147.5, 137.1, 137.0, 124.2, 123.5, 119.5, 118.2, 71.4, 47.5, 19.3, 18.6;

1-isopropyl-3,5-3,5-di(2'-pyridyl)-6-oxoverdazyl (1)

1-isopropyl-3,5-di(2'-pyridyl)-6-oxotetrazane (**4**) (0.148 g, 0.5 mmol) was dissolved in 4 mL of water and heated gently until all solids were dissolved. The tetrazane solution was cooled for approximately two minutes and then added to a solution of sodium periodate (0.16 g, 0.75 mmol) dissolved in approximately 3 mL of water. The solution immediately changed to a deep orange color and was stirred for 0.5 h. The resulting mixture was extracted with dichloromethane and the organic layer evaporated to give the free radical (0.15 g, 100%). EI-MS: m/z(relative intensity) 296(100, M+1), 197 (55), 121 (25), 105(25), 78 (35) IR (NaCl plate) 3061 2975 2928 1689 1588 1466 1369 1272 cm^{-1}; ESR (toluene) $a_{N2,4}$=0.66, a_{N1}=0.49, a_{N5}=0.43, a_H=0.15, $a_{N(pyridyl)}$=0.074 mT, g=2.0034, linewidth=0.075 mT; UV-vis (acetonitrile) λmax (ε) 404 (1060), 483 (530).

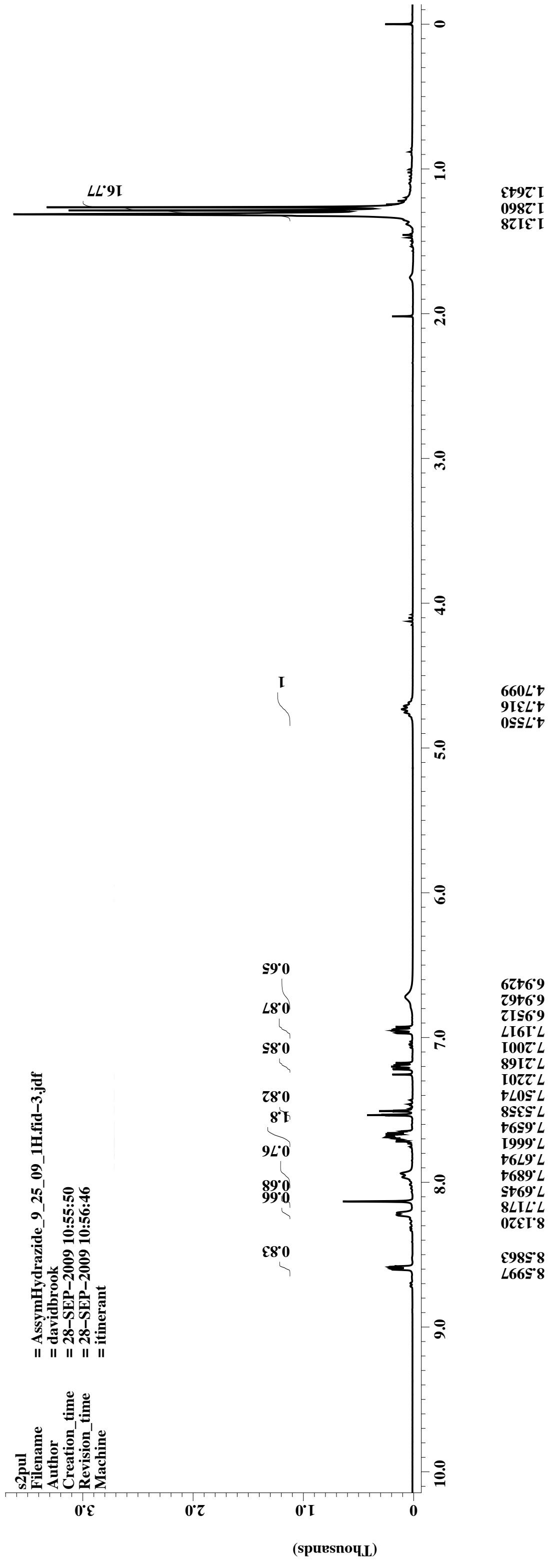
Bis(1-isopropyl-3,5-3,5-di(2'-pyridyl)-6-oxoverdazyl)nickel(II) hexafluorophosphate (5)

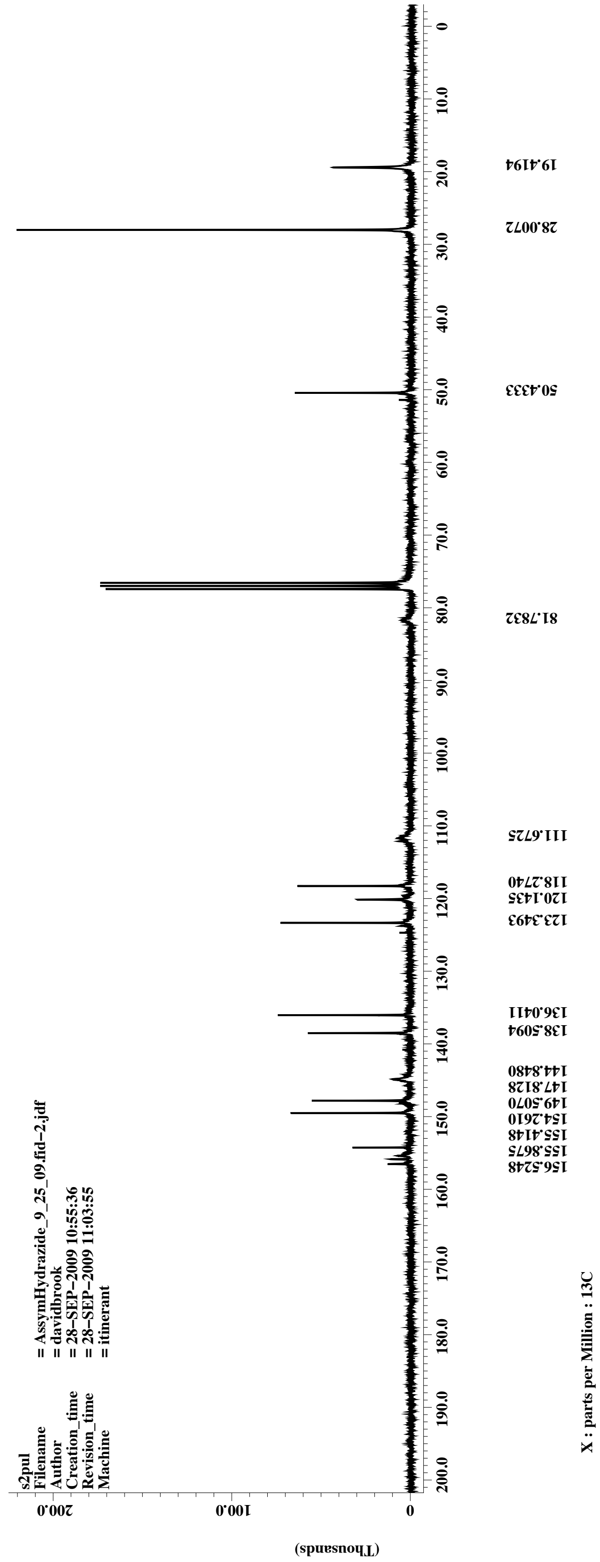
1-isopropyl-3,5-di(2'-pyridyl)-6-oxoverdazyl (0.15 g, 0.5 mmol) was dissolved in acetonitrile (2 mL). To this was added a solution of nickel triflate (0.133g, 0.25 mmol) also dissolved in acetonitrile (2 mL). An immediate red color was visible upon mixing and the solution was left to stand for five minutes. After evaporation of the solvent, the solution was redissolved in methanol and the hexafluorophosphate salt precipitated by addition of excess aqueous sodium hexafluorophosphate. After standing at 4°C for 0.5 h the product was isolated by gravity filtration to give a dark red solid (0.10 g, 42%). IR (NaCl plate) 1725 (C=O), 1599 (C=N) cm^{-1}, Electrospray MS: 648.2 (100) 649.2 (42) 650.2 (50) 651.2 (18) 652.2 (8.4) 653.2 (2.4); calcd for $[(C_{15}H_{15}N_6O)_2Ni]^+$ 648.2 (100) 649.2 (37) 650.2 (46) 651.2 (13) 652.2 (8.8) 653.2 (2); anal. C 37.33 H 3.01 N 17.73 calcd. for $[(C_{15}H_{15}N_6O)_2Ni]^{2+}(PF_6^-)_2 \cdot H_2O$ C 37.64 H 3.37 N 17.56, UV-vis (acetonitrile) λmax (ε) 585 (4600), 550 (3200), 513 (sh 1970), 453 (4500), 436 (sh 3900), 410 (4160) 376 (4490).

Magnetic Susceptibility was recorded on a sample of **5** (14.3 mg) mounted in a gelatin capsule and held in place with cotton wool. An external field of 5000 G was used to measure magnetization from 5 K to 300 K in a Quantum Design MPMS-5 SQUID magnetometer. Data were corrected for diamagnetism of the cotton and gelatin, along with sample diamagnetism (χ_{dia}= -4.3×10^{-4} $emu.mol^{-1}$ calculated using Pascal's constants). χT was fitted to the equation reported by Kahn[2] with an additional antiferromagnetic term $-zJ'$ to model the low temperature data. The best fit was determined by least squares with $J_{Ni\text{-}Vd}$, $J_{Vd\text{-}Vd}$, zJ' and g_{Ni} as parameters. g_{verd} was fixed at 2.00. The best fit gave $J_{Ni\text{-}Vd}$=+300 cm^{-1}, $J_{Vd\text{-}Vd}$=+160 cm^{-1}, zJ'=−1.21(4) cm^{-1}, g_{Ni}=2.035(2), with R=0.0011. However, the two exchange parameters are strongly correlated as described in the manuscript text.

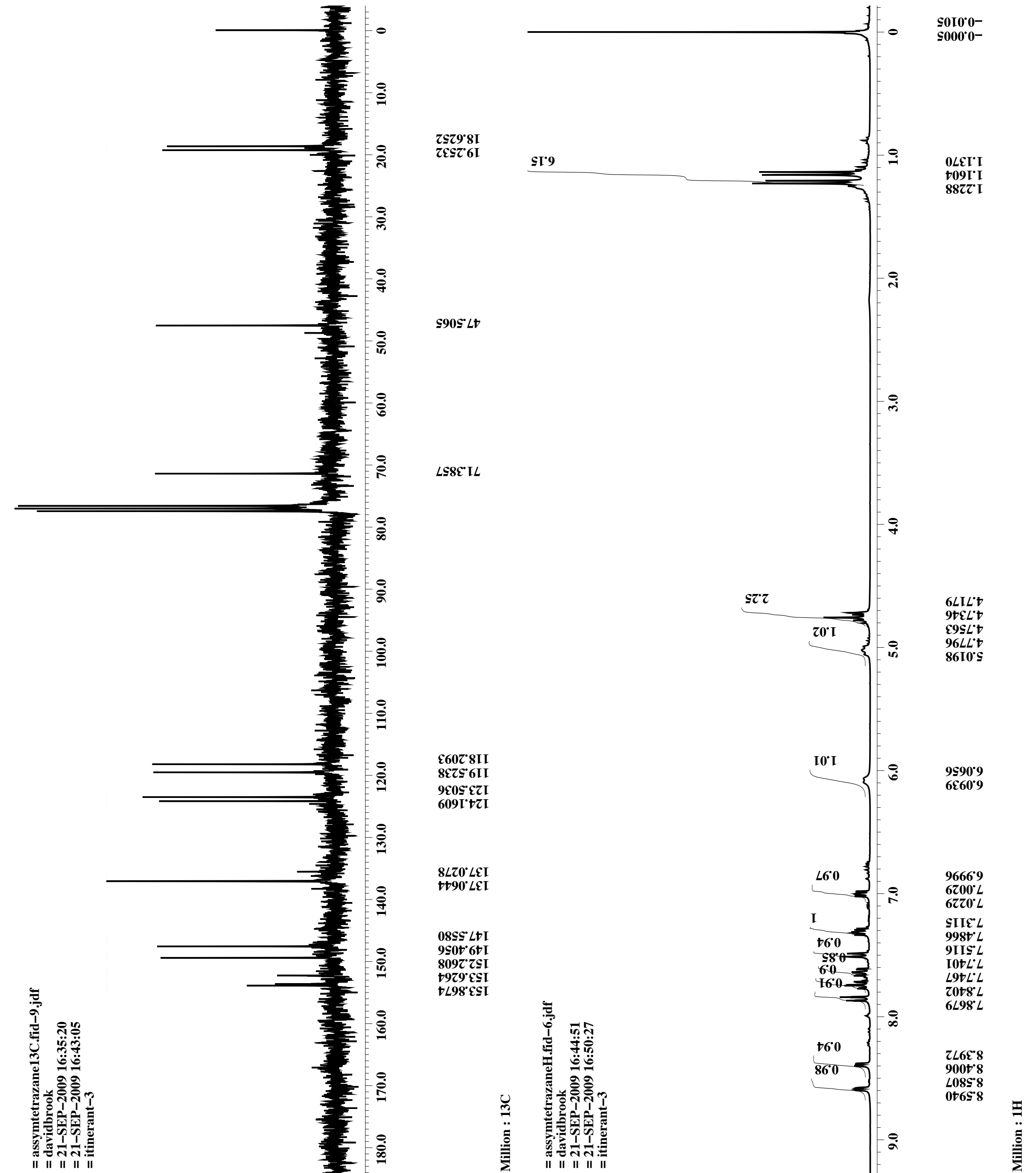
X-ray quality crystals with composition $[(C_{15}H_{15}N_6O)_2Ni]^{2+}(PF_6^-)_2$ were obtained by slow evaporation of a solution in acetone/ethanol. Details of data collection, solution and refinement in *cif* format have been deposited at the Cambridge Crystallographic Data Center, deposition number 753408.

^{1}H and ^{13}C NMR spectra for compound **3**





^{1}H and ^{13}C NMR spectra for compound **4**



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