Supplementary Information

Neutral acetohydroxamic acid coordination to a mononuclear Ni(II) center stabilized by a intramolecular hydrogen-bonding interaction

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Experimental Section

General and physical methods. Performed as previously described.[1]

Synthesis of ligand precursors. The organic precursors 2-(pivalolylamido)-6-(bromomethyl)pyridine,[2] 6-phenyl-2-pyridinecarboxyaldehyde,[3] 6-phenyl-2-pyridinemethanol[1] were prepared as previously reported.

(6-phenyl-2-pyridyl)methyl amine. A multistep synthetic procedure for the preparation of this compound from 6-phenyl-2-pyridinemethanol has been previously reported by Chuang, et al.[3] This literature procedure was followed for conversion of 6-phenyl-2-pyridinemethanol to 2-(chloromethyl)-6-phenylpyridine hydrochloride and conversion of this halide derivative to 2-(phthalimidomethyl)-6-phenyl pyridine. However, removal of the phthalimido protecting group was achieved via treatment of 2-(phthalimidomethyl)-6-phenyl pyridine (2.1 g, 6.5 mmol) with hydrazine monohydrate (0.42 g, 8.4 mmol) in ethanol (65 mL) solution. This reaction mixture was heated at reflux under a nitrogen atmosphere for two hours. After cooling the solution to room temperature, water (45 mL) and 1M HCl were added until a pH~2 was attained. The resulting cloudy solution was warmed gently for two hours. The reaction mixture was then allowed to cool to ambient temperature and was filtered. The yellow filtrate was treated with 1M NaOH until the pH~12. Extraction with CH_2Cl_2 (3 x 100 mL), followed by drying of the combined organic solutions over Na_2SO_4, filtration, and removal of the solvent under reduced pressure yielded a dark yellow oil (1.17 g, 98%). The ^{1}H NMR properties of the material in $CDCl_3$ matched those previously reported.[3]

***N,N*-bis((6-phenyl-2-pyridyl)methyl)-*N*-(((6-pivaolylamido)-2-pyridyl)methyl)amine (bppppa). Step 1.** To an ethanol solution (~5 mL) of (6-phenyl-2-pyridyl)methyl amine (0.72 g, 3.9 mmol) was added an ethanol solution (~5 mL) of 6-phenyl-2-pyridinecarboxyaldehyde (0.72 g, 3.9 mmol). The resulting yellow mixture was stirred at 45(1) °C for ~50 min. The solution was then cooled to room temperature and solid $NaBH_4$ (0.16 g, 4.7 mmol) was added at which point the solution color became orange. This mixture was stirred at ambient temperature for 24 h. To this solution was added 1 M HCl (~20 ml) until a pH~2 was reached. Following removal of all volatiles under reduced pressure, the resulting yellow-orange semisolid was treated with CH_2Cl_2 (~5 mL) and 1 M NaOH until the pH > 11. The organic portion was removed and the aqueous fraction was extracted with Et_2O (3 x 50 mL). The combined organic fractions were dried over excess Na_2SO_4, filtered, and evaporated to dryness yielding a brown oil (1.35 g). The major product in this oil has ^{1}H NMR properties consistent with the

formation of the reductive amination product *N,N*-bis(((6-phenyl)-2-pyridyl)methyl)amine (^{1}H NMR (CD_3CN, 400 MHz) δ 8.09-8.06 (m, 4H), 7.78 (t, J = 7.7 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H), 7.47-7.38 (m, 6H), 7.34 (d, J = 7.7 Hz, 2H) 4.03 (s, 4H); a N-H resonance was not identified). However, an impurity with a benzylic resonance at 4.71 ppm and aromatic resonances that partially overlap with the signals outlined above is consistently present in the product isolated using this reaction pathway. Thus far we have been unable to find reaction and/or column conditions that are suitable for the clean isolation of *N,N*-bis(((6-phenyl)-2-pyridyl)methyl)amine. However, the secondary amine product can be used in its crude form in a reaction to generate the bppppa ligand as described below.

Step 2. To a CH_3CN (50 mL) solution of 2-(pivalolylamido)-6-(bromomethyl)pyridine (0.33 g, 1.2 mmol) was added crude *N,N*-bis-(((6-phenyl)-2-pyridyl)methyl)amine (0.42 g, 1.2 mmol), Na_2CO_3 (0.50 g, 4.7 mmol) and ~5 mg of tetrabutylammonium bromide. The resulting mixture was heated at reflux under nitrogen for ~14 h. At this point, the reaction mixture was cooled to room temperature and 1 M NaOH (~50 mL) was added. The organic/aqueous mixture was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic fractions were dried over Na_2SO_4, filtered, and the organic solvent was removed under reduced pressure yielding a thick brown oil. This crude product was purified via column chromatography on silica gel (240-400 mesh, CH_2Cl_2:CH_3OH 10:1, R_f = 0.62; impurity with R_f = 0.65 could not be separated). The final sample was isolated as a pale yellow oil (0.33 g, 73%) and contains ~15% impurity (^{1}H NMR properties suggest a structure for this impurity involving the (6-phenyl-2-pyridyl)methyl fragment). Attempts to purify the bppppa ligand further using various column conditions have thus proven unsuccessful. However use of this impure ligand did not cause problems in metal complexation reactions (see preparation of **1** below). The bppppa ligand can be isolated free of the impurity via treatment of crystalline **1** with NaCN in methanol/water to remove the Ni(II) ion (66% recovery yield).[4] Characterization data was recorded for clean bppppa obtained from the metal complexation/removal strategy: ^{1}H NMR (CD_3CN, 400 MHz) δ 8.15 (br, 1H, N-H), 8.05-8.02 (m, 4H), 7.97 (d, J = 7.9 Hz, 1H), 7.78-7.74 (m, 2H), 7.71-7.67 (m, 3H), 7.54 (d, J = 7.5 Hz, 2H), 7.48-7.38 (m, 7H), 3.97 (s, 4H), 3.87 (s, 2H), 1.24 (s, 9H); $^{13}C\{^1H\}$ NMR (CD_3CN, 100 MHz) δ 178.0, 160.5, 159.5, 157.0, 152.3, 140.4, 139.6, 138.4, 129.9, 129.7, 127.8, 122.7, 119.6, 119.5, 112.7, 61.1, 60.9, 40.5, 27.6 (19 signals expected and observed); FTIR (neat, cm^{-1}): 1690 ($\nu_{C=O}$); LRFAB-MS (CH_2Cl_2:NBA) *m/z* (relative intensity): 542 ($[M+H]^+$, 100%). Anal. Calcd for $C_{35}H_{35}N_5O{\cdot}1.75H_2O$: C, 73.34; H, 6.77, N, 12.22. Found: C, 73.34; H, 6.39; N, 11.73. The presence of water in the sample was confirmed by ^{1}H NMR.

Caution! Perchlorate salts containing organic ligands are potentially explosive. These materials should be handled on a small scale and handled with great care.[5]

[(bppppa)Ni(HONHC(O)CH$_3$)](ClO$_4$)$_2$ (1). To a methanol solution (~2 mL) of bppppa (41 mg, 0.075 mmol) was added a methanol solution (~2 mL) of $Ni(ClO_4)_2 \cdot 6H_2O$ (27.6 mg, 0.075 mmol). The resulting mixture was stirred for 40 min at room temperature at which point a methanol solution (~1 mL) of acetohydroxamic acid (5.7 mg, 0.075 mmol) was added. The pale blue solution was then stirred for overnight at room temperature. At this point, the solvent was removed under reduced pressure. Recrystallization of the residue via Et_2O diffusion into a CH_3OH:CH_3CN (1:2.5) of the complex yielded purple crystals suitable for single crystal X-ray diffraction (48 mg, 72%). UV-vis (CH_3CN) [λ_{max}, nm (ε, $M^{-1}cm^{-1}$)]: 570 (15), 920 (20); FTIR (KBr, cm^{-1}) 1656 ($\nu_{C=O}$, bppppa amide); μ_{eff} = 3.3 μ_B (298 K); Anal. Calcd for $C_{37}H_{40}N_6O_{11}Cl_2Ni$: C, 50.91; H, 4.62; N, 9.63. Found: C, 50.51; H, 4.87; N, 9.49.

References

1. M. M. Makowska-Grzyska, E. Szajna, C. Shipley, A. M. Arif, M. H. Mitchell, J. A. Halfen, and L. M. Berreau, *Inorg. Chem.*, 2003, **42**, 7472.
2. L. M. Berreau, S. Mahapatra, J. A. Halfen, V. G. Young, Jr., and W. B. Tolman, *Inorg. Chem.*, 1996, **35**, 6339.
3. C-L. Chuang, K. Lim, Q. Chen, J. Zubieta, and J. W. Canary, *Inorg. Chem.*, 1995, **34**, 2562.
4. L. M. Berreau, M. M. Makowska-Grzyska, and A. M. Arif, *Inorg. Chem.*, 2000, **39**, 4390. (See electronic supporting information; section on isolation and identification of bmapa ligand).
5. W. L. Wolsey, *J. Chem. Educ.,* 1973, **50**, A335.

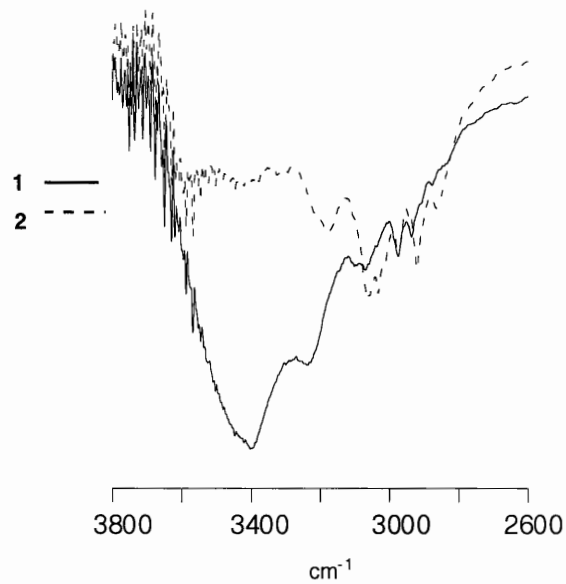

Figure S1(a). 3800-2600 cm^{-1} region of the infrared spectra of **1** and **2**.

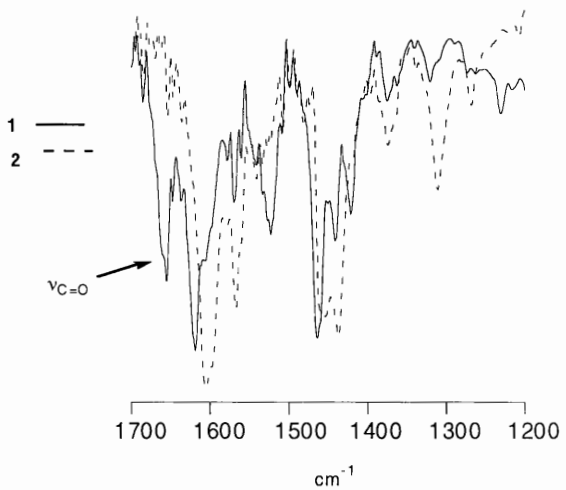

Figure S1(b). 1700-1200 cm^{-1} region of the infrared spectra of **1** and **2**.

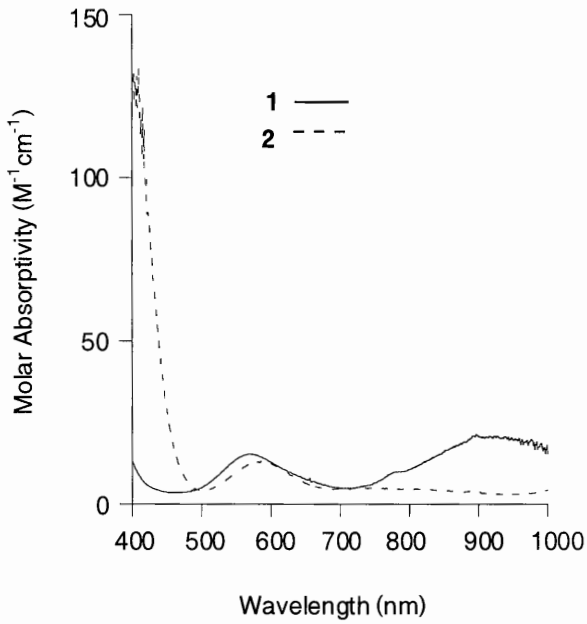

Figure S2. Electronic absorption spectra of **1** and **2** in dry CH_3CN. The feature for **2** that extends into the UV range is a shoulder that is centered at ~372 nm (ε ~ 330 M^{-1} cm^{-1}).