Supporting Information

Mononuclear Nitrogen/Sulfur-ligated Zinc Methoxide and Hydroxide Complexes:
Investigating Ligand Effects on the Hydrolytic Stability of Zinc Alkoxide Species

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Experimental Procedures.

General.

All reagents and solvents were obtained from commercial sources and were used as received unless otherwise noted. Solvents were dried according to published procedures\(^1\) and were distilled under N\(_2\) prior to use. All reactions leading to the formation and isolation of the zinc complexes reported herein were performed in a MBraun Unilab glovebox under an atmosphere of purified dry N\(_2\).

Physical Methods. \(^1\)H and \(^{13}\)C\(^{\text{1}}\)H\) NMR spectra were recorded at 20(1) °C on a JEOL GSX-270 or Bruker ARX-400 spectrometer. Chemical shifts (in ppm) are referenced to a residual solvent peak(s) in CD\(_3\)CN (\(^1\)H: 1.95 (quintet); \(^{13}\)C\(^{\text{1}}\)H\): 1.39 (heptet) ppm). FTIR spectra were recorded on a Shimadzu FTIR-8400 spectrometer as KBr pellets or as neat oils between NaCl plates. Electron impact ionization mass spectra were obtained at the University of California, Riverside, using a VG 7070 low-resolution mass spectrometer operating in the positive ion mode. Elemental analyses were performed by Atlantic Microlabs of Norcross, GA.

Synthesis and Characterization of Ligands and Complexes.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared and these should be handled with great care.\(^2\)

**N-2-(ethylthio)ethyl-N,N-bis(6-pivaloylamido-2-pyridylmethyl)amine** (ebppa). To a solution of 2-pivaloylamido-6-bromomethylpyridine\(^3\) (6.23 g, 0.023 mol) in CH\(_3\)CN (100 mL) were added 2-(ethylthio)ethylamine hydrochloride (1.63 g, 0.012 mol), sodium carbonate (5.09 g), and tetrabutylammonium bromide (~5 mg). The resulting mixture was heated at reflux under N\(_2\) for 24 h. After cooling to room temperature, the reaction mixture was poured into 1 M NaOH (100 mL). The resulting solution was extracted with CH\(_2\)Cl\(_2\) (3 x 125 mL), the combined organic fractions were
dried over Na₂SO₄, and the solution was brought to dryness under reduced pressure. Column chromatography on silica gel (2:1 ethyl acetate:hexane, 200-400 mesh silica gel, Rᵣ ~ 0.30 (broad, trailing band); impurity observed at Rᵣ ~ 0.65) yielded a pale yellow oil (4.17 g, 75%). ¹H NMR (CD₃CN, 270MHz) δ 8.17 (br, 2H, N-H), 7.99 (d, J = 8.2 Hz, 2H), 7.71 (t, J = 7.7 Hz, 2H), 7.30 (d, J = 7.5 Hz, 2H), 3.72 (s, 4H), 2.80-2.60 (m, 4H), 2.45 (q, J = 7.3 Hz, 2H), 1.27 (s, 18H), 1.15 (t, J = 7.3 Hz, 3H); LREI-MS, m/z (relative intensity): 487 ([M+H]⁺, 15%).

N-2-(ethylthio)ethyl-N,N-bis(6-neopentylamino-2-pyridylmethyl)amine (ebnpa). To a 500 mL round bottom flask was added 2.2 g (58 mmol) LiAlH₄ followed by a solution of 45 mL dry pyridine in 200 mL dry THF. To this solution was added 4.2 g (8.6 mmol) of ebppa dissolved in 40 mL of dry THF. The resulting solution was heated at reflux with stirring under N₂ for 18 h. After cooling the reaction mixture to room temperature, an equal volume of water was added, with the initial addition being done dropwise to minimize vigorous bubbling and emulsion formation. Extraction of the mixed organic/aqueous reaction mixture with ethyl acetate (4 x 200 mL), followed by drying of the combined organic fractions with Na₂SO₄, filtration, and removal of volatile solvents under reduced pressure, yielded a thick yellow-orange oil. The analytically pure ebnpa ligand was isolated following column chromatography (2:1 ethyl acetate:hexane, 200-400 mesh silica gel, maximum Rᵣ ~ 0.78 (broad, trailing band)) as a clear, pale yellow oil (1.95 g, 50%). ¹H NMR (CD₃CN, 270MHz) δ 7.33 (t, J = 7.6 Hz, 2H), 6.70 (d, J = 7.2 Hz, 2H), 6.33 (d, J = 8.2 Hz, 2H), 5.00 (br, 2H, N-H), 3.60 (s, 4H), 3.14 (d, J = 6.6 Hz, 4H), 2.80-2.60 (m, 4H), 2.45 (q, J = 7.3 Hz, 2H), 1.20 (t, J = 7.3 Hz, 3H), 0.93 (s, 18H); ¹³C [¹H] NMR (CD₃CN, 67.9 MHz) δ 160.1, 158.7, 138.1, 111.6, 106.2, 60.9, 54.7, 53.4, 32.9, 29.8, 27.8, 26.4, 15.4 (13 signals expected and observed); FTIR (neat, cm⁻¹) ~3350 (br, ν₅–H); LREI-MS, m/z (relative intensity): 458 ([M+H]⁺, 20%). Anal Calcd. for C₂₉H₄₅N₅S: C, 68.23; H, 15.30; N, 9.47. Found: C, 67.77; H, 15.11; N, 9.51.
[(ebnpa)Zn(OCH₃)]ClO₄ (1). To a solution of ebnpa (113 mg, 0.248 mmol) in dry methanol (2 mL) was added solid Zn(ClO₄)₂·6H₂O (90 mg, 0.24 mmol). The resulting mixture was stirred for ~30 minutes at which time all of the Zn(ClO₄)₂·6H₂O had gone into solution. The reaction mixture was then transferred to a glass vial containing solid Me₄NOH·5H₂O (46 mg, 0.25 mmol) and the resulting mixture was stirred for ~12 h. At this time, the solvent was removed under reduced pressure and the remaining solid was extracted with CH₂Cl₂ (3 x 2 mL). The combined solution extracts were filtered through a glass wool/celite plug and the volume of the filtrate was reduced to ~0.5 mL under reduced pressure. A white solid was precipitated from the solution by the addition of diethyl ether (~16 mL). After settling for 6 hours the solution was decanted and the solid dried under reduced pressure. Recrystallization of the solid from CH₂OH·Et₂O at -20°C yielded the product as champagne-colored crystals suitable for X-ray diffraction analysis (75 mg, 47%). ¹H NMR (CD₃CN, 270MHz) δ 10.37 (t, J = 2.6 Hz, 2H), 7.58 (t, J = 7.8 Hz, 2H), 6.63 (d, J = 8.9 Hz, 2H), 6.48 (d, J = 6.9 Hz, 2H), 3.86 (d, J = 15.2 Hz, 2), 3.72 (s, 3H), 3.60 (d, J = 15.2 Hz, 2H), 3.00 (d, J = 5.9 Hz, 4H), 2.91-2.80 (m, 4H), 2.41 (q, J = 7.3 Hz, 2H), 1.25 (t, J = 7.3 Hz, 2H), 1.02 (s, 18H); ¹³C{¹H} NMR (CD₃CN, 100.6MHz): δ 162.2, 152.5, 142.1, 111.2, 107.7, 57.0, 55.5, 53.3, 49.6, 33.1, 27.8, 27.7, 25.2, 14.3 (14 signals expected and observed); FTIR (KBr, cm⁻¹) 3251 (v₉H), 1093 (vClO₄), 623 (vClO₄). Anal Calcd. for C₁⁷H₂⁸N₂O₅SCl: C, 49.75; H, 7.12; N, 10.75. Found: C, 49.31; H, 6.76; N, 10.79.

[(ebnpa)Zn(OH)]ClO₄ (2). To a solution of ebnpa (98 mg, 0.21 mmol) in dry acetonitrile (~2 mL) was added solid Zn(ClO₄)₂·6H₂O (76 mg, 0.21 mmol). The resulting mixture was stirred for ~10 minutes at which time all of the Zn(ClO₄)₂·6H₂O had gone into solution. The reaction mixture was then transferred to a glass vial containing solid Me₄NOH·5H₂O (37 mg, 0.20 mmol) and the resulting mixture was stirred for ~12 h. At this time, the solvent was removed under reduced pressure and the remaining solid was extracted with CH₂Cl₂ (3 x 5 mL). The combined solution extracts were filtered through a
glass wool/celite plug and the filtrate was brought to dryness under reduced pressure. Recrystallization of the remaining solid from CH$_3$CN:Et$_2$O at ambient temperature yielded the product as champagne-colored crystals suitable for X-ray diffraction analysis (105 mg, 81%). $^1$H NMR (CD$_3$CN, 270MHz) $\delta$ 10.97 (t, $J = 6.6$ Hz, 2H), 7.57 (t, $J = 7.5$ Hz, 2H), 6.58 (d, $J = 8.9$ Hz, 2H), 6.45 (d, $J = 6.9$ Hz, 2H), 3.83 (d, $J = 15.2$ Hz, 2H), 3.58 (d, $J = 15.2$ Hz, 2H), 3.00 (dd, $J = 12.8$, $J = 5.2$, 2H), 2.94 (dd, $J = 12.8$, $J = 5.2$, 2H), 2.91-2.84 (m, 4H), 2.46 (q, $J = 7.3$ Hz, 2H), 1.72 (s, 1H), 1.26 (t, $J = 7.3$ Hz, 3H), 1.03 (s, 18H); $^{13}$C ($^1$H) NMR (CD$_3$CN, 67.9MHz): $\delta$ 160.8, 152.3, 142.3, 112.2, 108.2, 58.2, 55.0, 51.9, 33.0, 28.4, 27.5, 25.6, 13.9 (13 signals expected and observed); FTIR (KBr, cm$^{-1}$) 3600 (v$_{O-H}$), 1325 (v$_{C=O}$), 1090 (v$_{C=O}$), 623 (v$_{Cl=O}$). Anal Calcd. for C$_{26}$H$_{44}$N$_3$O$_5$ZnCl: C, 48.96; H, 6.96; N, 10.99. Found: C, 49.17; H, 6.95; N, 10.92.

**X-ray Crystallography.** Crystals of compounds 1 and 2 were mounted on a glass fiber with traces of viscous oil and then transferred to a Nonius KappaCCD diffractometer with Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) for data collection and 200(1) K. For each compound, an initial set of cell constants was obtained from ten frames of data that were collected with an oscillation range of 1 deg/frame and an exposure time of 20 sec/frame. Final cell constants for each complex were determined from a set of strong reflections from the actual data collection. For each data set, these reflections were indexed, integrated, and corrected for Lorentz, polarization, and absorption effects using DENZO-SMN, SCALEPAC, and Multi-scan. Each structure was solved by a combination of direct methods and heavy atom using SIR97. All of the non-hydrogen atoms were refined with anisotropic displacement coefficients. Unless otherwise noted, hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(Cmethyl), and their coordinates were allowed to ride on their respective carbons using SHELXL97.

**Structure Solution and Refinement.** Crystals of 1 were determined to belong to the triclinic crystal system. Systematic absences in the data for the zinc methoxide
complex [(ebnpa)ZnOCH₃]ClO₄ (1) were consistent with the space group P-1. In 1, two
formula units are present in the asymmetric unit, with the second being denoted by an
“A” designation. A molecule of methanol is also present in the asymmetric unit.
Hydrogen atoms were located and refined independently except those on O(6), C(11A),
C(12A), C(13A), C(14A), and C(28), which were assigned isotropic displacement
coefficients, and their coordinates were allowed to ride on their respective atoms (oxygen
or carbon). The carbon atoms of one neopentyl moiety exhibit disorder. These carbon
atoms (C(11A), C(12A), and C(14A)) were each split into two fragments (second
fragment denoted by a prime) and were refined. This refinement led to a 0.83:0.17 ratio
in occupancy over two positions for each carbon atom. The hydroxide complex 2
crystallizes in the space group P2₁/n. Hydrogen atoms were located and refined
independently except those on C(22), C(24), and C(25), which were assigned isotropic
displacement coefficients, and their coordinates were allowed to ride on their respective
carbon atoms.

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Figure S1. $^1$H NMR spectrum

$$[(ebnpa)Zn(OCH_3)]ClO_4$$

(1)

$S = CD_3CN$

$* = diethylether$

Temp = 304 K
Figure S2. $^1$H NMR spectrum of [(ebnpa)Zn(OH)]ClO$_4$ (2)

$S = CD_3CN$

Temp = 304 K
Figure S3. $^1$H NMR spectrum of equilibrium mixture

$[(\text{ebn} \text{p} \text{a})\text{Zn(OH)}]\text{ClO}_4 + \text{CH}_3\text{OH} \xrightleftharpoons{K_{Me}} [(\text{ebn} \text{p} \text{a})\text{Zn(OCH}_3\text{)}]\text{ClO}_4 + \text{H}_2\text{O}$

(2)  

S = CD$_3$CN
Temp = 300 K

(1), OCH$_3$
(2), OH
(1), NH
(2), NH

ppm
Figure S4. Representative van't Hoff plot for Zn-OH/Zn-OCH₃ equilibrium

van't Hoff Plot for the equilibrium

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\begin{align*}
(2) \quad [(\text{ebnpa})\text{Zn(OH)}]\text{ClO}_4 + \text{CH}_3\text{OH} & \quad \Leftrightarrow \quad [(\text{ebnpa})\text{Zn(OCH}_3)]\text{ClO}_4 + \text{H}_2\text{O} \\
(1) & \quad K_{Me} \\
\Delta H &= -0.9(1) \text{ kcal/mol} \quad \Delta S = -5(1) \text{ eu}
\end{align*}
\]

\[
y = 418.8x - 2.6096 \\
R^2 = 0.9968
\]