
A New Synthesis of *Bis*(2-{pyrid-2-yl}ethyl)amine (L^H) from *Bis*(2-{pyrid-2-yl}ethyl)hydroxylamine (L^{OH}), and the Copper-Dependent Reduction of L^{OH} to L^H †

Stewart A. Leaver^a, Mallayan Palaniandavar^b, Colin A. Kilner^a and Malcolm A. Halcrow^{*a}.

^a*School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, U.K. LS2 9JT.*

Email: M.A.Halcrow@chem.leeds.ac.uk

^b*Department of Chemistry, Bharathidasan University, Tiruchirapalli 620024, India.*

Solutions of $[CuCl_2L^{OH}]$, and other reaction mixtures containing L^{OH} and Cu(II) or Cu(I) salts, rapidly degrade to yield dark green or brown residues containing the L^H ligand. In contrast, $[MCl_2L^{OH}]$ ($M = Zn, Ni, Co$) are indefinitely stable in solution and the solid state.

Electronic Supplementary Information

Full synthetic procedures and analytical data for the ligands and complexes in this study.

EXPERIMENTAL PROCEDURES FOR THE COMPOUNDS IN THIS STUDY

All manipulations were performed in air using commercial grade reagents and solvents.

Synthesis of bis(2-(pyrid-2-ylethyl)hydroxylamine) (L^{OH}). A modification of the literature procedure was followed.^{7,8} Commercial 2-vinylpyridine was purified by dissolution in CH₂Cl₂, filtration of the solution through a silica plug, and removal of the solvent. To the resultant pale yellow oil (50 g, 0.47 mol) was added NH₂OH.HCl (24.5 g, 0.35 mol), and the mixture was allowed to stand at room temperature overnight, affording a gel. This was neutralised with aqueous NaHCO₃, and the product extracted from the mixture with CHCl₃. The organic washings were dried over MgSO₄ and evaporated to dryness. Recrystallisation of the residue from CH₂Cl₂/hexanes yielded pale yellow feathery microcrystals. These can be handled in air, but slowly darken upon storage at room temperature over a period of weeks. Yield 51.0 g, 60 %. (Found: C, 69.1; H, 7.1; N, 17.5; Calcd. for C₁₄H₁₇N₃O: C, 69.1; H, 7.0; N, 17.3 %). EI mass spectrum: *m/z* 243 [L^{OH}]⁺, 226 [L^{OH}-OH]⁺, 135 [L^{OH}-OH-pyCH]⁺, 106 [pyC₂H₄]⁺, 92 [pyCH₂]⁺. NMR spectra (CDCl₃, 293K): ¹H; δ 8.37 (dd, 4.9 and 1.9 Hz, 2H, Py H⁶), 7.99 (br s, 1H, OH), 7.50 (pseudo-td, 7.6 and 1.9 Hz, 2H, Py H⁴), 7.10 (d, 7.8 Hz, 2H, Py H³), 7.04 (ddd, 7.6, 4.9 and 1.1 Hz, 2H, Py H⁵), 3.03 (s, 8H, CH₂). ¹³C; δ 160.4 (Py C²), 149.1 (Py C⁶), 136.4 (Py C⁴), 123.3, 121.1 (Py C³ + C⁵), 60.0 (CH₂NOH), 36.0 (CH₂Py).

Synthesis of bis(2-(pyrid-2-ylethyl)amine hemihydrate) (L^H.½H₂O). A mixture of L^{OH} (50 g, 0.21 moles) and zinc powder (67.3 g, 1.0 mol) in 2N HCl (250 cm³) was stirred at 85°C for 1 hr. After cooling, the solution was adjusted to pH 10 using concentrated aqueous ammonia, and the resultant mixture extracted twice with CH₂Cl₂. The organic washings were dried over MgSO₄ and evaporated to dryness, leaving a pale yellow oil that was analysed without further purification. Yield 42.0 g, 90 %. (Found: C, 71.6; H, 7.5; N, 17.9; Calcd. for C₁₄H₁₇N₃.½H₂O: C, 71.2; H, 7.7; N, 17.8 %). EI mass spectrum: *m/z* 227 [L^H]⁺, 135 [L^H-pyCH₂]⁺, 121 [pyC₂H₄NH]⁺, 106 [pyC₂H₄]⁺, 92 [pyCH₂]⁺. NMR spectra (CDCl₃, 293K): ¹H; δ 8.41 (d, 6.5 Hz, 2H, Py H⁶), 7.48 (pseudo-td, 7.6 and 1.8 Hz, 2H, Py H⁴), 7.01 (m, 4H, Py H³ + H⁵), 5.21 (s, 1H, NH), 2.85 (m, 8H, CH₂), 1.94 (s, 1H, OH₂). ¹³C; δ 160.2 (Py C²), 149.3 (Py C⁶), 136.2 (Py C⁴), 123.2, 121.1 (Py C³ + C⁵), 49.2 (CH₂NH), 38.3 (CH₂Py).

Synthesis of [bis(2-(pyrid-2-ylethyl)hydroxylamine)dichlorocopper(II)] ([CuCl₂L^{OH}], 1). A mixture of L^{OH} (0.25 g, 1.0 x 10⁻³ mol) and CuCl₂.2H₂O (0.18 g, 1.0 x 10⁻³ mol) in MeNO₂ (30 cm³) was stirred at room temperature for 5 mins. The resultant green solution was filtered, and concentrated *in vacuo* without heating to half its original volume. Slow addition of Et₂O to the solution afforded a blue-green precipitate which was collected, washed with Et₂O and dried *in vacuo*. Yield 0.14 g, 35 %. (Found: C, 44.6; H, 4.6; N, 10.9; Calcd. for C₁₄H₁₇Cl₂CuN₃O: C, 44.5; H, 4.5; N, 11.1 %). FAB mass spectrum: *m/z* 341 [⁶³Cu³⁵ClL^{OH}]⁺, 306 [⁶³CuL^{OH}]⁺ with correct isotopic distributions. UV/vis/NIR (CH₂Cl₂): ν_{max}, x10⁻³ cm⁻¹ (ε_{max}, M⁻¹.cm⁻¹) 9.8 (119), 14.1 (228), 30.1 (sh), 34.2 (4,800), 36.9 (sh), 38.6 (10,100), 39.9 (sh). IR (nujol): 3129 br, 1606s, 1569m, 1492s, 1441s, 1320m, 1156m, 1112m, 1025m, 896m, 885m, 778m, 769s, 760s, 728m, 649m, 558s cm⁻¹. X-band powder EPR (120 K): g₁ = 2.21, g₂ = 2.13, g₃ = 2.00, no resolved hyperfine coupling.

Synthesis of [bis(2-(pyrid-2-ylethyl)hydroxylamine)dichlorocopper(II)] ([CuCl₂L^H], 2). This complex was prepared by the published method.^{3,7} (Found: C, 46.5; H, 4.8; N, 11.5; Calcd. for C₁₄H₁₇Cl₂CuN₃: C, 46.5; H, 4.7; N, 11.6 %). FAB mass spectrum: *m/z* 325 [⁶³Cu³⁵ClL^H]⁺, 290 [⁶³CuL^H]⁺ with correct isotopic distribution. UV/vis/NIR (CH₂Cl₂): ν_{max}, x10⁻³ cm⁻¹ (ε_{max}, M⁻¹.cm⁻¹) 9.6 (sh), 13.0 (203), 20.8 (100), 21.8 (sh), 30.8 (sh), 35.1 (sh), 36.9 (sh), 37.9 (10,780), 38.4 (sh). IR (nujol): 1608s, 1568m, 1484m, 1315m, 1160m, 1115m, 1086m, 1027m, 1008m, 926m, 789m, 778s, 764s, 722m, 649m, 601m cm⁻¹. X-band powder EPR (120 K): g₁ = 2.16, g₂ = 2.11, g₃ = 2.01, no resolved hyperfine coupling.

Synthesis of [bis(2-(pyrid-2-ylethyl)hydroxylamine)dichlorozinc(II)] ([ZnCl₂L^{OH}], 3). A mixture of L^{OH} (0.25 g, 1.0 x 10⁻³ mol) and ZnCl₂.2H₂O (0.18 g, 1.0 x 10⁻³ mol) in MeOH (30 cm³) was stirred at room temperature for 10 mins. The resultant dark yellow solution was filtered, and allowed stored at -30°C. The resultant tan crystals were collected, washed with Et₂O and dried *in vacuo*. Yield 0.16 g, 42 %. (Found: C, 44.4; H, 4.5; N, 11.0; Calcd. for C₁₄H₁₇Cl₂N₃OZn: C, 44.3; H, 4.5; N, 11.1 %). FAB mass spectrum: *m/z* 342 [⁶⁴Zn³⁵ClL^{OH}]⁺ with correct isotopic distribution. NMR spectrum (CD₂Cl₂, 293K): ¹H; δ 8.60 (2H, Py H⁶), 8.24 (s, 1H, NOH), 7.80 (td, 7.8 and 1.8 Hz, 2H, Py H⁴), 7.35 (m, 4H, Py H³ + H⁵), 3.41 (br m, 8H, CH₂). UV/vis/NIR (CH₂Cl₂): ν_{max}, x10⁻³ cm⁻¹ (ε_{max}, M⁻¹.cm⁻¹) 34.7 (sh), 37.3 (8,500), 38.0 (8,100). IR (nujol): 3393 br, 1609s, 1569m, 1488s, 1445s, 1358m, 1315m, 1286m, 1159m, 1107m, 1062m, 1047m, 1027m, 991m, 907m, 791m, 772m, 767s, 754m, 741m, 667m, 651m, 636m cm⁻¹.

Synthesis of [bis(2-(pyrid-2-ylethyl)hydroxylamine)dichloronickel(II)] ([NiCl₂L^{OH}], 4). Method as for **3**, using NiCl₂.6H₂O (0.24 g, 1.0 x 10⁻³ mol). The product formed blue-green microcrystals from MeOH. Yield 0.24 g, 64 %. (Found: C, 44.9; H, 4.4; N, 11.1; Calcd. for C₁₄H₁₇Cl₂N₃NiO: C, 45.1; H, 4.6; N, 11.3 %). FAB mass spectrum: *m/z* 707 [⁵⁸Ni³⁵Cl₂L^{OH}]⁺, 336 [⁵⁸Ni³⁵ClL^{OH}]⁺ with correct isotopic distributions. NMR spectrum (CD₂Cl₂, 293K): ¹H; δ 173.0 (2H, Py H⁶), 51.7, 38.9 (both 2H, Py H³ + H⁵), 41.9 (1H, NOH), 25.6 (2H, Py H⁴), 0.9 (4H, CH₂), -17.5 (2H, CH₂), -21.5 (2H, CH₂). UV/vis/NIR (CH₂Cl₂): ν_{max}, x10⁻³ cm⁻¹ (ε_{max}, M⁻¹.cm⁻¹) 5.7 (12), 8.7 (23), 13.1 (sh), 15.8 (50), 25.3 (155), 32.3 (sh), 37.9 (8,500), 38.8 (8,400). IR (nujol): 3181m, 1607s, 1571m, 1486m, 1441s, 1309m, 1162m, 1147m, 1109m, 1059m, 1019m, 893m, 782m, 769s, 746s, 667m, 643m cm⁻¹.

Synthesis of [bis(2-(pyrid-2-ylethyl)hydroxylamine)dichlorocobalt(II)] ([CoCl₂L^{OH}], 5). Method as for **3**, using CoCl₂.6H₂O (0.24 g, 1.0 x 10⁻³ mol). The product formed purple crystals from MeOH. Yield 0.21 g, 56 %. (Found: C, 45.3; H, 4.5; N, 11.1; Calcd. for C₁₄H₁₇Cl₂CoN₃O: C, 45.1; H, 4.6; N, 11.3 %). FAB mass spectrum: *m/z* 337 [⁵⁹Co³⁵ClL^{OH}]⁺ with correct isotopic distribution. NMR spectrum (CD₂Cl₂, 293K): ¹H; δ 164.7 (2H, Py H⁶), 44.8, 42.6 (both 2H, Py H³ + H⁵), 23.2 (2H, Py H⁴), 7.4 (1H, NOH), 4.9 (2H, CH₂), -29.2 (2H, CH₂), -30.2 (2H, CH₂), -44.6 (2H, CH₂). UV/vis/NIR (CH₂Cl₂): ν_{max}, x10⁻³ cm⁻¹ (ε_{max}, M⁻¹.cm⁻¹) 6.0 (15), 10.5 (10), 14.0 (sh), 16.4 (sh), 17.3 (81), 18.6 (89), 21.6 (35), 36.8 (sh), 37.7 (7,300). IR (nujol): 3180m, 1605s, 1567m, 1492s, 1439s, 1315m, 1154m, 1109m, 1053m, 1015s, 987m, 893m, 794m, 784m, 768s, 762s, 726m, 648m, 640m cm⁻¹.

*Thermal decomposition of $[\text{CuCl}_2\text{L}^{\text{OH}}]$ (**1**).* An solution of **1** (0.38 g, 1.0×10^{-3} mol) in CH_2Cl_2 (50 cm^3) was allowed to stand at room temperature for two days. The resultant dark brown solution showed the following UV/vis/NIR spectrum: ν_{max} , $\times 10^{-3} \text{ cm}^{-1}$ (ϵ_{max} , $\text{M}^{-1} \cdot \text{cm}^{-1}$) 10.5 (sh), 14.2 (350), 20.3 (sh), 21.1 (422), 30.8 (sh), 34.4 (5,530), 37.0 (sh), 38.5 (11.4), 40.2 (sh). The solution was filtered and evaporated to dryness, yielding a dark green solid that was analysed without further purification. FAB mass spectrum: m/z 325 $[\text{}^{63}\text{Cu}^{35}\text{ClL}^{\text{H}}]^+$, 290 $[\text{}^{63}\text{CuL}^{\text{H}}]^+$, 228 $[\text{HL}^{\text{H}}]^+$ with correct isotopic distribution. IR (nujol): 1607s, 1568m, 1484m, 1317m, 1159m, 1109m, 1086m, 1027m, 1007m, 923m, 788m, 773s, 722m, 650m, 604m cm^{-1} . X-band powder EPR (120 K): $g_1 = 2.17$, $g_2 = 2.11$, $g_3 = 2.01$, no resolved hyperfine coupling. The remainder of the dark green product was stirred in concentrated aqueous ammonia (20 cm^3), until the solution turned deep blue. The solution was extracted with CH_2Cl_2 ($2 \times 50 \text{ cm}^3$), and the washings were dried over MgSO_4 . Evaporation of the solution to dryness afforded a pale yellow oil, whose ^1H NMR spectrum showed the presence of $\text{L}^{\text{H}} \cdot \frac{1}{2}\text{H}_2\text{O}$ (see above), together with ca. 20% of unidentified byproduct(s).