Synthesis of L1 and L2

L1 and L2 were synthesised by oximation\(^1\) of their aldehyde precursors.\(^2\)

**5-tert-Butyl-3-dihexylaminomethyl-2-hydroxybenzaldehyde oxime (L1).**

Potassium hydroxide (1.42 g, 25 mmol) and hydroxylamine hydrochloride (1.80 g, 26 mmol) were mixed in ethanol (300 ml) and a white KCl precipitate was removed by filtration. The filtrate was added to 5-tert-butyl-3-dihexylaminomethyl-2-hydroxybenzaldehyde\(^2\) (8.56 g, 23 mmol) in ethanol (1 l), stirred for 3 h and the solvent removed in vacuo to give a tarry yellow solid (7.57 g, 85%) which was used without further purification. (Found: C, 73.9; H, 10.5; N, 7.0. C\(_{24}\)H\(_{42}\)N\(_2\)O\(_2\) requires C, 73.8; H, 10.8; N, 7.2%); \(\delta\)\(^H\) (250 MHz; CDCl\(_3\); Me\(_4\)Si): 0.80 (t, 6H, 2 x N(CH\(_2\))\(_2\)C\(_{3}\)H\(_3\)), 1.21 (m, 21H, C(C\(_3\)H\(_3\))\(_3\) + 2 x N(CH\(_2\))\(_2\)C\(_3\)H\(_6\)CH\(_3\)), 1.55 (m, 4H, 2 x NCH\(_2\)CH\(_2\)C\(_4\)H\(_9\)), 2.56 (m, 4H, 2 x NC\(_2\)H\(_2\)C\(_5\)H\(_{11}\)), 3.83 (s, 2H, ArC\(_2\)H\(_2\)N), 7.20 (s, 1H, ArH), 7.40 (s, 1H, ArH), 8.33 (s, 1H, ArCH\(_2\)N); \(\delta\)\(^C\) (63 MHz; CDCl\(_3\); Me\(_4\)Si): 14.5 (N(CH\(_2\))\(_5\)C\(_{3}\)H\(_3\)), 22.5 (N(CH\(_2\))\(_4\)C\(_{2}\)H\(_3\)CH\(_3\)), 26.0 (N(CH\(_2\))\(_3\)C\(_2\)H\(_2\)C\(_3\)H\(_7\)), 27.5 (N(CH\(_2\))\(_2\)CH\(_2\)C\(_2\)H\(_7\)), 31.5 (C(C\(_3\)H\(_3\))\(_3\)), 32.0 (NCH\(_2\)CH\(_2\)C\(_4\)H\(_11\)), 34.0 (C(CH\(_3\))\(_3\)), 53.0 (NCH\(_2\)CH\(_2\)H), 58.0 (ArC\(_2\)H\(_2\)N), 117.6 (ArC), 122.0 (ArC), 122.5 (ArCH), 127.5 (ArCH), 142.0 (Ar), 147.9 (ArCHN), 154.6 (Ar); MS (FAB, NOBA): \(m/z\) 391 (MH\(^+\), 100%).

**Solvent Extraction – Metal Salt Extraction and Transport**

A 0.01 M solution of L1 in chloroform (5 ml) was contacted with a 1 M metal salt aqueous solution (5 ml) and stirred for 16 hrs. The organic phase was extracted, a 0.5 ml aliquot taken to be used for metal/sulfur analysis by ICP-OES and a 2.0 ml aliquot taken for chloride analysis. In copper stripping experiments, the remainder of the organic phase was contacted with HCl solutions of varying concentrations (5 ml) and stirred for 16 hr. The organic phase was extracted and a 0.5 ml aliquot taken for copper analysis.
Chloride concentration was measured by stirring the 2 ml aliquot of the organic phase with 10 ml of 0.1 M HNO₃ overnight, to strip all chloride ions into the aqueous phase. After separation, a 4 ml aliquot was contacted with 1 ml of a stock solution of AgNO₃ (0.02 M) to precipitate the chloride as AgCl. The mixture was centrifuged and filtered through a 0.2 µm single-use syringe filter, and a 2 ml aliquot of the filtrate was made up to 10 ml in a volumetric flask to measure the remaining silver concentration by ICP-OES. Chloride loading values were calculated from the concentration of Ag⁺ ions remaining in solution, with each loading value an average of two runs and corrected from values obtained by blank solutions.

**Dependence of Cu uptake on [Cl⁻]**

A 0.01 M solution of L₁ in chloroform (5 ml) was contacted with an aqueous phase consisting of 1 ml of 0.05M aqueous CuCl₂ and 4 ml of a mixture of aqueous 2 M NaCl and water to vary the chloride concentration. This ensured a 1:1 ratio of L₁:Cu throughout the experiment. The organic phase was extracted, a 0.5 ml aliquot taken for Cu analysis and the equilibrium pH of the aqueous phase measured. A plot of copper loading against aqueous chloride concentration illustrates the trend, showing maximum copper loading of ~180% when chloride concentration ≥ 0.8 M.

![Graph](image)

**Fig 1** Dependence of CuⅡ loading by L₁ on chloride concentration when a 0.01 M chloroform solution of L₁ was contacted with a 0.01 M solution of CuCl₂, with [Cl⁻] adjusted by addition of NaCl. Loading values are based on a 2:1 ligand to CuCl₂ ratio, equilibrium pH values were measured and all fell in the range 2.6-2.9.

**Hydrolytic Stability**

The hydrolytic stabilities of L₁, L₂ and some related compounds were determined by contacting 0.01 M solutions of each compound (10 ml) with 0.8 M aqueous H₂SO₄/Na₂SO₄ solutions (10 ml) of varying pH for a period of 16 hours. The organic
layer was separated, dried with MgSO₄ and then concentrated \textit{in vacuo}. The product was then analysed by $^1$H NMR spectroscopy, and the integrals of the imine proton and aldehyde proton were compared to evaluate the extent of hydrolysis of the ligand, with percentage degradation plotted against equilibrium pH of the aqueous phase after extraction (Figure 2).

\textbf{Fig 2} Percentage degradation of L₁, L₂ and some related metal salt extractants when a 0.01 M chloroform solution was contacted with a 0.8 M aqueous solution of H₂SO₄/Na₂SO₄ of varying pH.

The "salen" type metal salt extractant (green) starts to degrade at pH \textasciitilde3 and shows almost complete hydrolysis when the pH of the aqueous phase is 2.5. In contrast, L₁ (black) and L₂ (red) show little degradation at pH 1.5, and their related 5-nonyl analogue (maroon) shows almost no hydrolysis at pH 0.5, in similar fashion to the commercial reagent P50 (5-nonyl-2-hydroxybenzaldehyde oxime, blue).