Experimental

2-Hydroxy-5-nonylbenzaldehyde. (1)

Magnesium turnings (7.30 g, 0.30 mol), methanol (142 ml), toluene (56 ml) and magnesium methoxide (1.60 g of an 8% w/w solution in methanol) were stirred at reflux for 2 hrs until all the magnesium had dissolved and evolution of hydrogen had ceased. 4-Nonylphenol (112 g, 0.51 mol) was added and the mixture heated at reflux for 1 h. Toluene (120 ml) was added and the methanol-toluene azeotrope removed by distillation at reduced pressure until the temperature became constant. A slurry of paraformaldehyde (45.0 g, 1.50 mol) in toluene (75 ml) was added over 50 min with concurrent removal of volatile products by distillation under reduced pressure. Heating was continued for 2 hrs until the reaction mixture became very thick, then allowed to cool to room temperature. 20% sulfuric acid (625 ml) was added slowly and the mixture heated at 50 °C for 2 hrs when the thick toffee-like material had dispersed evenly. The mixture was allowed to cool and extracted with toluene (2 × 115 ml). The combined organic layers were washed with 10% sulfuric acid (50 ml), water (50 ml), separated and dried over anhydrous magnesium sulfate, and the volatiles removed under vacuum. The crude product was obtained as a pale yellow oil, which was partially purified via column chromatography using 20:1 hexane: ethyl acetate (R_f = 0.51) to give *2-hydroxy-5-nonyl-benzaldehyde* (82.1 g, 65%); ν_{max}/cm^{-1} (KBr cell) 3193 (O-H), 2732-2959 (C-H), 1658 (C=O); (Anal. Calc. for $C_{16}H_{24}O_2$: C, 77.4; H, 9.7%; Found: C, 78.1; H, 10.0%); ^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 11.12 (s, 1H, Ar-O*H*) 10.11 (s, 1H, C*H*=O), 7.68 (m, 2H, Ar-*H*), 7.15 (d, 1H, Ar-*H*), 0.72-2.00 (m, 19H, C_9H_{19}); ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm) 196.6 (1C, *C*HO), 159.1 (1C, Ar-*C*), 139.1-141.8 (1C, Ar-*C*C_9H_{19}), 134.7-135.5 (1C, Ar-*C*H), 130.3-131.2 (1C, Ar-*C*H), 119.8 (1C, Ar-*C*), 116.9 (1C, Ar-*C*H), 8.3-52.0 (9C, C_9H_{19}); *m/z* 248 $(M)^+$.

2-Hydroxy-5-nonylbenzylidene octanehydrazide L^2H_2.

A solution of (1) (10.1 g, 41 mmol) and octanoic hydrazide (6.52 g, 41 mmol) in acetonitrile (150 ml) was stirred at reflux for 16 hrs. The mixture was allowed to cool to room temperature and the solvent removed *in vacuo* to give a dark brown, viscous oil. This was purified by column chromatography on silica using 80:20 hexane: ethyl acetate (R_f = 0.91) to yield *2-hydroxy-5-nonylbenzylidene)octanehydrazide* (12.8 g, 81%); λ_{max} /nm ($CHCl_3$) 330 (11154), 292 (28862), 282 (31958); ν_{max}/cm^{-1} (KBr cell) 3203 (O-H), 3055 (N-H), 2871-2957 (C-H), 1662 (C=O), 1625 (C=N), 1558 (N-H), 1277 (C-N) (Anal. Calc. for $C_{24}H_{40}N_2O_2$: C, 74.18; H, 10.38; N, 7.21%; Found: C, 74.27; H, 10.25; N, 6.90 %); ^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 10.70 (s, 1H, N*H*), 10.21 (s, 1H, Ar-O*H*), 8.01 (s, 1H, C*H*N), 7.21 (m, 2H, Ar-*H*), 6.91 (d, ^3J = 8.6 Hz, Ar-*H*), 2.65 (t, 2H, CHOCH_2C$_6$H$_{13}$), 0.48-1.75 (m, 32H, C_9H_{19}, CHOCH$_2$C$_6H_{13}$); ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm) 176.1 (1C, *C*HO), 155.2 (1C, Ar-*C*), 148.4 (1C, *C*HN), 139.0-141.7 (1C, Ar-*C*C_9H_{19}), 128.3-130.2 (2C, 2Ar-*C*H), 116.6 (1C, Ar-*C*), 116.0 (1C, Ar-*C*H), 8.4-51.5 (16C, C_9H_{19}, C_7H_{15}); *m/z* 388 $(M)^+$.

2-Hydroxy-3-nitro-5-nonylbenzaldehyde. (2)

Nitric acid (2.81 ml, 63 mmol) was added drop wise to a solution of 2-hydroxy-5-nonyl-benzaldehyde (10.0 g, 40 mmol) in glacial acetic acid (25 ml) at 0 °C. The mixture heated to 55 °C and stirred for 16 hrs, then allowed to cool to room temperature. Excess acid was removed *in vacuo* with gentle heating to yield a bright yellow oil, which was purified via column chromatography using 80:20 hexane: diethyl ether (R_f = 0.59) to yield *2-hydroxy-3-nitro-5-nonyl-benzaldehyde* (10.5 g, 89%); ν_{max}/cm^{-1} (KBr cell) 3212 (O-H), 2767-2964 (C-H), 1667-1695 (C=O); (Anal. Calc. for $C_{16}H_{23}NO_4$: C, 65.5; H, 7.9; N, 4.8%; Found: C, 64.3; H, 7.8; N, 4.8%); ^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 11.16 (s, 1H, Ar-O*H*), 10.27 (s, 1H, C*H*=O), 8.15 (m, 1H, Ar-*H*), 7.97 (m, 1H, Ar-*H*), 0.37-1.68 (m, 19H, C_9H_{19}); ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm) 189.2 (1C, *C*HO), 153.9 (1C, Ar-*C*), 140.1-142.6 (1C, Ar-*C*C_9H_{19}), 134.3-135.0 (1C, Ar-*C*H), 128.1-128.8 (1C, Ar-*C*H), 124.5 (1C, Ar-*C*), 124.3 (1C, Ar-*C*), 8.0-50.6 (9C, *C*$_9$H$_{19}$); *m/z* 292 $(M-H)^-$.

2-Hydroxy-3-nitro-5-nonylbenzylidene octanehydrazide L^3H_2.

A solution of (2) (7.01 g, 24 mmol) and octanoic hydrazide (3.78 g, 24 mmol) in acetonitrile (200 ml) was stirred at reflux for 16 hrs. The mixture was allowed to cool to room temperature and the solvent removed *in vacuo* to give a dark brown, viscous oil, which was purified by column chromatography using 80:20 hexane: ethyl acetate (R_f = 0.42) to yield *2-hydroxy-3-nitro-5-nonyl-benzaldehyde-octanoylhydrazone* (10.2 g, 98%); ν_{max}/cm^{-1} (KBr cell) 3205 (O-H), 3054 (N-H), 2872-2960 (C-H), 1669 (C=O), 1626 (C=N), 1533 (N-H), 1265 (C-N); (Anal. Calc. for $C_{24}H_{39}N_3O_4$: C, 66.48; H, 9.07; N, 9.69 %; Found: C, 66.30; H, 8.89; N, 9.54 %); ^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 10.97 (s, 1H, Ar-O*H*), 10.07 (s, 1H, N*H*), 8.2 (s, 1H, C*H*N), 8.00 (m, 2H, Ar-*H*), 2.73 (t, 2H, CHOC*H*$_2$C$_6$H$_{13}$), 0.68-1.74 (m, 32H, C$_9$*H*$_{19}$, CHOCH$_2$C$_6$*H*$_{13}$); ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm) 176.1 (1C, *C*HO), 150.6 (1C, Ar-*C*), 144.5 (1C, Ar-*C*), 139.5 (1C, *C*HN), 134.1-134.8 (1C, Ar-*C*C_9H_{19}), 132.0 (1C, Ar-*C*H), 123.0-123.8 (1C, Ar-*C*H), 122.0 (1C, Ar-*C*), 7.9-43.8 (16C, *C*$_9$H$_{19}$, *C*$_7$H$_{15}$); *m/z* 434 $(MH)^+$.

2-Hydroxy-5-*t*-butylbenzaldehyde. (3)

2-Hydroxy-5-*tert*-butyl-benzaldehyde was prepared in a similar manner to 2-hydroxy-5-nonyl-benzaldehyde, using 4-*t*-butylphenol (200 g, 1.30 mol). The yellow oil obtained was purified by column chromatography on silica gel, eluting with 5% ethyl acetate in hexane. The solution was dried *in vacuo* to yield a yellow oil (150 g, 65%); ν_{max}/cm^{-1} (neat) 3200 (OH), 1698 (C=O), 1515 (Ar C=C), 1395 (^{t}Bu CH_3); ^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 10.69 (s, 1H, O*H*), 9.71 (s, 1H, C*H*O), 7.41 (d, 1H, *J* 2.5 Hz, Ar*H*), 7.34 (d, 1H, *J* 2.5 Hz, Ar*H*), 6.76 (d, 1H, *J* 8.6 Hz, Ar*H*), 1.12 (s, 9H, (C*H*$_3$)$_3$C); ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm) 196.7 (1C, *C*HO), 159.4 (1C, Ar-*C*), 142.6 (1C, Ar-*C*), 134.6 (1C, Ar-*C*), 129.6 (1C, Ar-*C*), 119.9 (1C, Ar-*C*), 117.1 (1C, Ar-*C*), 33.9 (1C, *C*$(CH_3)_3$), 31.1 (3C, C(*C*H_3)$_3$); *m/z* 179 $(MH)^+$.

4-*t*-Butyl-2-{[(*E*)-5-*t*-butyl-2-hydroxy-phenylimino]methyl}-phenol L^4H_2.

A solution of 2-amino-4-*t*-butylphenol (2.00 g, 12.1 mmol) and 2-hydoxy-5-*t*-butylbenzaldehyde (3) (2.20 g, 12.1 mmol) in methanol (50 ml) was stirred for 4 hrs. The resulting yellow solid was collected by filtration and a second crop obtained by reducing the mother liquor to *ca.* 10 ml. The product is obtained by filtration as an orange solid. Recrystallisation from methanol yielded orange crystals suitable for crystallography (1.90 g, 49%); ν_{max}/cm^{-1} (nujol) 3153 (OH), 1624 (N=C), 1376 (^{t}Bu CH_3); (Anal. Calc. for $C_{21}H_{27}NO_2$ (crystals ground and dried): C, 77.5; H, 8.4; N, 4.3. Found: C, 77.2; H, 8.7; N, 4.3%); ^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 8.90 (s, 1H, ArC*H*N), 7.69-7.64 (m, 2H, 2 x Ar*H*), 7.45 (dd, 1H, *J* 8.5, 2.3 Hz, Ar*H*), 7.34 (d, 1H, *J* 2.3 Hz, Ar*H*), 7.20 (d, 1H, *J* 8.5 Hz, Ar*H*), 7.16 (d, 1H, *J* 8.5 Hz, Ar*H*), 1.27 (s, 18H, 2 x C(CH_3)$_3$); ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm) 163.9 (1C, Ar*C*HN), 158.2 (1C, Ar-*C*), 147.3 (1C, Ar-*C*), 143.9 (1C, Ar-*C*), 142.2 (1C, Ar-*C*), 135.1 (1C, Ar-*C*), 131.0 (1C, Ar-*C*), 128.9 (1C, Ar-*C*), 125.4 (1C, Ar-*C*), 118.5 (1C, Ar-*C*), 116.7 (1C, Ar-*C*), 115.1 (2C, Ar-*C*), 34.3 (1C, *C*(CH_3)$_3$), 33.9 (1C, *C*(CH_3)$_3$), 31.4 (3C, C(*C*H_3)$_3$), 31.3 (3C, C(*C*H_3)$_3$); *m/z* 326 $(MH)^+$.

3-Formyl-2-hydroxy-5-methylbenzoic acid. (4)

5-Methylsalicylic acid (5.5 g, 36 mmol) was dissolved in trifluoroacetic acid (50 ml). Hexamethylenetetramine (15.5 g, 110 mmol) was added and the resulting mixture heated to 100 ^{o}C for 16 hrs. Without cooling the solution was poured into an aqueous solution of hydrochloric acid (150 ml, 1 M) and stirred for 16 hrs. The resulting yellow precipitate was washed with cold water and dried *in vacuo*, recrystallised from water/ethanol to yield *3-formyl-2-hydroxy-5-methylbenzoic acid* (4.09 g, 63%); ν_{max}/cm^{-1} (KBr cell) 3448 (ArO-H), 3060 (COO-H), 1687 (C=O), 1262 (C-OOH); (Anal. Calc. for $C_9H_8O_4$: C, 60.00; H, 4.48. Found: C, 59.96; H, 4.31%); ^{1}H NMR (250 MHz, DMSO) δ_H (ppm) 10.30 (s, 1H, C*H*=O), 7.85 (d, 1H, Ar-*H*), 7.67-7.66 (d , 1H, Ar-*H*), 2.25 (s, 3H, Ar-C*H*$_3$). ^{13}C NMR (63 MHz, DMSO) δ_C (ppm) 188.39 (1C, *C*H=O), 171.63 (1C, *C*OOH), 161.54 (1C, Ar-*C*-OH), 136.97 (1C, Ar-*C*H), 133.75 (1C, Ar-*C*H), 128.18 (1C, Ar-*C*), 123.46 (1C, Ar-*C*), 114.11 (1C, Ar-*C*), 19.66 (1C, *C*H_3). *m/z* 179 $(M-H)^-$.

3-((2-Octanoylhydrazono)-methyl)-5-methylsalicylic acid L^5H_3.

A suspension of (4) (1.80 g, 10 mmol), octanoic hydrazide (1.58 g, 10 mmol) and anhydrous magnesium sulphate in chloroform (50 ml) was warmed to 40 ^{o}C and stirred for 16 hrs. The mixture was filtered to remove unreacted starting material and magnesium sulphate, and washed with cold chloroform. The filtrate was evaporated to dryness then *in vacuo* to yield *3-((2-octanoylhydrazono)-methyl)-5-methylsalicylic acid* (2.91 g, 91%). (Anal. Calc. for $C_{17}H_{24}N_2O_4$: C, 63.73; H, 7.55; N, 8.74%; Found: C, 63.42; H, 7.94; N, 8.65%); ^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 11.36 (s (br), 1H, COO*H*), 11.05 (s, 1H, Ar-O*H*), 7.95 (s, 1H, C*H*N), 7.54 (d, 1H, Ar-*H*), 7.42 (d ,

1H, Ar-*H*), 2.58 (t, 2H, C=OC*H*$_2$), 2.19 (s, 3H, Ar-C*H*$_3$), 1.67-1.59 (m, 2H, C*H*$_2$), 1.37-1.23 (m, 8H, (C*H*$_2$)$_4$), 0.94-0.83 (m, 3H, C*H*$_3$). ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm) 178.48 (1C, *C*OOH), 174.53 (1C, NH*C*=O), 159.08 (1C, Ar-*C*-OH), 140.84 (1C, *C*H=N), 133.06 (1C, Ar-*C*H), 131.67 (1C, Ar-*C*H), 127.78 (1C, Ar-*C*), 121.30 (1C, Ar-*C*-CH=N), 112.30 (1C, Ar-*C*-OOH), 32.02 (2C, Alk-*C*H$_2$), 29.71 (1C, Alk-*C*H$_2$), 29.42 (1C, Alk-*C*H$_2$), 24.50 (1C, Alk-*C*H$_2$), 22.93 (1C, Alk-*C*H$_2$), 20.68 (1C, Ar-*C*H$_3$), 14.35 (1C, Alk-*C*H$_3$); *m/z* 321 $(MH)^+$.

3-((5-*tert*-Butyl-2-hydroxyphenylamino)methyl)-5-methylsalicylic acid L^6H_3.

(4) (1.80 g, 0.01 mol) and 2-amino-4-*tert*-butyl-phenol (1.65 g, 0.01 mol) were stirred in methanol (100 ml) for 1 h. A deep red precipitate formed on contact. This was filtered and washed with cold methanol and dried *in vacuo* to yield *3-((5-tert-butyl-2-hydroxyphenylamino)methyl)-2-hydroxy-5-methylbenzoic acid* (3.26 g, 99.7%). (Anal. Calc. for $C_{19}H_{21}NO_4$: C, 69.71; H, 6.47; N, 4.28; Found: C, 68.97; H, 6.40; N, 4.16%); ^{1}H NMR (250 MHz, DMSO) δ_H (ppm) 10.77 (s, 1H, COO*H*), 9.43 (s, 1H, C*H*N), 7.98-7.97 (d , 1H, Ar-*H*), 7.82-7.81 (d, 1H, Ar-*H*), 7.64-7.63 (d, 1H, Ar-*H*), 7.32-7.28 (dd, 1H, Ar-*H*), 7.01-6.97 (dd, 1H, Ar-*H*), 2.56 (s, 3H, C*H*$_3$), 1.31 (s, 9H, (C*H*$_3$)$_3$). ^{13}C NMR (63 MHz, DMSO) δ_C (ppm) 173.53 (1C, *C*OOH), 167.50 (1C, Ar-*C*-OH), 158.39 (1C, *C*HN), 146.79 (1C, Ar-*C*-OH), 142.91 (1C, Ar-*C*), 140.98 (1C, Ar-*C*H), 139.62 (1C, Ar-*C*H), 126.72 (1C, Ar-*C*H), 124.32 (1C, Ar-*C*), 130.05 (1C, Ar-*C*), 118.86 (1C, AR-*C*), 116.21 (1C, Ar-*C*), 116.07 (1C, Ar-*C*H), 114.70 (1C, Ar-*C*H), 34.28 (1C, *C*(CH$_3$)$_3$), 31.21 (3C, C*(CH$_3$)$_3$*), 19.58 (1C, *C*H$_3$). *m/z* 328 $(MH)^+$.

Dinuclear copper complex of 3-((5-tert-butyl-2-hydroxyphenylamino)methyl)-5-methylsalicylic acid L^6H_3.

A single crystal was obtained by layering a DMF solution of 3-((5-tert-butyl-2-hydroxyphenylamino)methyl)-5-methylsalicylic acid L^6H_3 on an aqueous copper sulfate solution after several weeks in the fridge.

Crystal data for $[Cu_2(L^6H)_2]$ (Figure 5)

Data were collected on a 3 circle Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and equipped with an Oxford Cryosystems low temperature device operating at 150 K. The crystal was indexed using the Cell_now indexing program[1] and found to be triclinic with *a* = 6.8829(7), *b* = 9.6493(10), *c* = 12.3771(12) Å and *α* = 88.498(6), *β* = 83.850(6), γ = 83.339(6) °. The crystal was also twinned and the twin law obtained after global cell refinement was

(-0.99434 -0.00064 -0.02085)
(0.00755 -0.99936 -0.01644)
(-0.43677 -0.05385 0.99478).

From initial indexing a data collection strategy was refined which aimed to collect fully complete data to a resolution of 53° in 2θ in as short a time as possible. In total 3802 reflections were collected and from these the space group was determined to be *P*-1. Absorption correction was performed using a multi-scan method by applying the

TWINABS[2] program to the data. The initial solution was determined by direct methods with the SHELXS[3] program. All heavy atoms were refined anisotropically and hydrogen atoms were placed geometrically and allowed to ride on their host atom. Full matrix least squares refinement was carried out against F^2 producing a final conventional R-Factor of 0.0865 based on 3091 reflections.

2,2-Dimethyl-propanoic hydrazide. (5)

Sodium hydroxide (12.9 g, 323 mmol) was dissolved in water (400ml). Hydrazine monohydrate (20.8 g, 400 mmol) added and the mixture cooled (*ca.* 0 to -5°C). Trimethylacetylchloride (38.6 ml, 320 mmol) was added drop wise and the temperature maintained at *ca.* 0 to -5°C over the duration *ca.* 1 h. The mixture was concentrated (ca. 100ml) by rotary evaporation **(Caution!)** and resulting solution filtered. The filtrate was collected and toluene added (100 ml). Water was removed by Dean-Stark apparatus and volume of the resulting solution reduced (*ca.* 40 ml) and filtered. *2,2-Dimethyl-propanoic hydrazide* precipitated as a white microcrystalline solid on cooling (7.78 g, 67.1 mmol), yield = 21.0%. (Anal. Calc. for $C_5H_{12}N_2O$: C, 51.70; H, 10.41; N, 24.12%; Found: C, 51.94; H, 10.84; N, 23.74); ^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm) 7.43(s (br), 1H, N*H*), 3.85 (s (br), 2H, NH_2), 1.14 (s, 9H, C$(CH_3)_3$); ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm) 179.34 (1C, *C*=O), 38.05 (1C, *C*$(CH_3)_3$), 27.41 (3C, C(*C*$H_3)_3$); *m/z* 117.1 $(MH)^+$.

(2-Hydroxy-5-methylbenzylidene)pivalohydrazide. (6)

2-Hydroxy-5-methylbenzaldehyde (1.36 g, 10 mmol) and (5) were dissolved in dichloromethane (100 ml). The resulting mixture heated under reflux for 3 hrs. The resulting solution was reduced in volume (*ca*. 30 ml). (2-hydroxy-5-methylbenzylidene)pivalohydrazide crystallised upon cooling as a white crystalline solid (1.53 g, 65%). (Anal. Calc. for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.74; N, 11.96%; Found: C, 66.41; H, 7.91; N, 11.65); ^{1}H NMR (250 MHz, DMSO) δ_H (ppm) 11.52 (s (br), 1H, COO*H*), 8.84 (s, 1H, C*H*N), 7.58 (s , 1H, Ar-*H*), 7.43-7.39 (dd, 1H, Ar-*H*), 7.16-7.13 (d, 1H, Ar-*H*), 2.57 (s, 3H, CH_3), 1.54 (s, 9H, $(CH_3)_3$). ^{13}C NMR (63 MHz, DMSO) δ_C (ppm) 173.65 (1C, *C*OOH), 155.36 (1C, Ar-*C*-OH), 147.46 (1C, *C*HN), 131.77 (1C, Ar-*C*H), 129.46 (1C, Ar-*C*H), 127.72 (1C, Ar-*C*), 118.31 (1C, Ar-*C*), 116.26 (1C, Ar-*C*H), 37.71 (1C, *C*$(CH_3)_3$), 27.08 (3C, C$(CH_3)_3$), 19.97 (1C, *C*H_3). *m/z* 235 $(MH)^+$.

Dinuclear copper complex of (2-hydroxy-5-methylbenzylidene)pivalohydrazide.

(6) (0.24 g, 1.0 mmol) and copper acetate (0.27 g, 1.1 mmol) were stirred in ethanol for 6 hrs. The resulting green precipitate was filtered, washed with water and ethanol, dried *in vacuo* and recrystallised from a minimum of chloroform to yield the dinuclear copper complex (0.27 g, 91.5%). (Anal. Calc. for $C_{26}H_{32}Cu_2N_4O_4$: C, 52.78; H, 5.45; N, 9.47%; Found: C, 52.41; H, 4.83; N, 9.07). *m/z* 591 $(MH)^+$.

Crystal data for $[Cu_2L_2].2CHCl_3$ (Figure 4)

Data were collected on a 3 circle Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) equipped with an Oxford Cryosystems low temperature device operating at 150 K. The crystal was indexed using the Bruker Smart software[4] and found to be triclinic with *a* = 5.9794(3), *b* = 9.9352(5), c = 15.3792(9) Å, and *α* = 98.853(4), β = 94.933(4), γ = 103.343(4) °. From initial indexing a data collection strategy was refined which aimed to collect fully complete data to a resolution of 53° in 2θ in as short a time as possible. In total 8149 reflections were collected and from these the space group was determined to be *P*-1. Absorption correction was performed using a multi-scan method by applying the SADABS[5] program to the data. The data were merged according to the crystal system in SHELX[3] which gave 3052 unique reflections with a merging R-factor of 0.0442. The initial solution was determined by direct methods with the SHELXS[3] program. All heavy atoms were refined anisotropically and hydrogen atoms were placed geometrically and allowed to ride on their host atom. Full matrix least squares refinement was carried out against F^2 producing a final conventional R-Factor of 0.0957 based on 2750 reflections.

Solvent Extraction Experiments

Example extraction conditions for $\mathbf{L^4}H_2$

Loading experiments were carried out in sealed glass jars. A solution of known concentration (0.00250 M) of $\mathbf{L^4}H_2$ in chloroform (5.0 ml) was contacted with an aqueous solution (5.0 ml). The aqueous solution contained 4.0 ml of metal salt solution ($CuSO_4$, 0.003125 M in water) and 1.0 ml of varied concentrations of NaOH or H_2SO_4 solutions to obtain the desired pH and a constant metal salt concentration equivalent to that of the ligand. The mixtures were stirred for 16 hrs at room temperature, and the organic and aqueous layers allowed to separate. A 1.00 ml aliquot was removed from the organic layer, evaporated *in vacuo*, redissolved and made up to 10.0 ml in butan-1-ol. The metal content was analysed using ICP-OES. The equilibrium pH of the aqueous layer was measured and the loading in the organic phase was expressed as the percentage of the total metal in the system present in the organic.

EPR analysis

Following determination of loading of copper by ICP-OES, a number of points (usually seven) that represented an even distribution between the highest and lowest copper(II) extractions were selected for EPR analysis. Samples from the organic phase were analysed and these were taken directly from the freshly separated extraction experiments. Each spectrum was recorded with a modulation of 4, the variable parameters used for each ligand system are shown in Table 2.

Ligand System	Centre Field (G)	Sweep Width (G)	Gain	Frequency (GHz)	Power (mW)	Sweep Time (s)
Ligand **1**	3000	700	8000	9.72	34	500
Ligand **1** + L_{aux}	3300	700	4000	9.71	32	500
Ligand **2** + L_{aux}	3320	500	100000	9.72	32	100

Table 2: EPR parameters.

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