

Supplementary Information

Synthesis:

[Cu(C₈H₁₇NH)₂sar](ClO₄)₂.xHClO₄

[Cu(NH₂)₂sar](OAc)₂ was prepared by dissolving (NH₂)₂sar•2H₂O (0.20 g, 0.57 mmol) and Cu(OAc)₂•4H₂O (0.14 g, 0.57 mmol) in EtOH (*ca.* 10 mL) and reducing the solution to dryness on the rotary evaporator. The blue [Cu(NH₂)₂sar](OAc)₂ and NaBH₃CN (0.16 g, 2.5 mmol) were dissolved in EtOH (*ca.* 20 mL) containing molecular sieves (3 Å, *ca.* 0.5 g), and the mixture heated at reflux before acetic acid (0.5 mL) was added, followed by the dropwise addition of octanal (0.50 mL, 3.2 mmol) in EtOH (*ca.* 10 mL). The reaction was allowed to proceed for 30 min, after which time the reaction mixture was cooled, then decanted and quenched by the addition of conc. HClO₄, producing a blue precipitate which was collected and washed with cold MeOH. The blue solid was dissolved in the minimum volume of MeCN, the mixture filtered to remove white insoluble material, and the product precipitated by the addition of MeOH/Et₂O to give [Cu(C₈H₁₇NH)₂sar](ClO₄)₂.xHClO₄ (0.20 g) as a waxy semicrystalline solid.

ESMS *m/z* 700.48 = [CuC₃₀H₆₆N₈ + ClO₄]⁺; 321.27 = [CuC₃₀H₆₆N₈ + CH₃CN]²⁺; 341.79 = [CuC₃₀H₆₆N₈ + 2CH₃CN]²⁺.

[Cu(C₇H₁₅NH)₂sar]Cl₂.xHCl and [Cu{(C₇H₁₅)₂N}(C₇H₁₅NH)sar]Cl₄.xHCl

[Cu(NH₂)₂sar](OAc)₂ (1.54 g, 3.1 mmol) was prepared as above for [Cu(C₈H₁₇NH)₂sar](ClO₄)₂.xHClO₄, and dissolved in EtOH (*ca.* 50 mL) in a two necked 100 mL flask equipped with a reflux condenser connected to a nitrogen line. Molecular sieves (3 Å, *ca.* 2 g) were added and the blue mixture stirred for *ca.* 5 min before heptanal (8.6 mL, 62 mmol) was added to the flask. After allowing the mixture to stir for a further 5 min, glacial acetic acid (0.25 mL) was added, followed by NaBH₃CN (0.44 g, 7.0 mmol), which produced some effervescence. The solution was then stirred for 18 h at RT under an atmosphere of nitrogen, before more NaBH₃CN (0.30 g, 4.8 mmol) was added, and the mixture heated at reflux for 24 h under nitrogen. The final mixture was allowed to cool to room temperature, filtered through a pad of Celite, and conc. HCl added to the filtrate causing vigorous effervescence, and the solvent removed on the rotary evaporator, to give a green/blue solid. The solid was extracted with CH₂Cl₂ (3 x 100 mL), the organic extracts discarded, and the solid dissolved in MeOH and applied to a column of silica. The mixture was then subjected to purification by rapid silica gel filtration by gradient elution with MeOH/DCM. This produced a leading brown band, followed by two, partially separated, blue bands. The first blue band was isolated using a 7.5% MeOH/DCM mixture, a middle fraction consisting of both bands was also collected and then the second band removed from the silica using 15% MeOH/DCM. Bands 1 and 2 were then brought to dryness on the rotary evaporator, and separately dissolved in MeOH and adsorbed onto columns of H⁺ Dowex 50Wx2 cation exchange resin. After washing with H₂O, 1 M HCl and MeOH (500 mL each), the complex was removed from the column using a mixture of conc. HCl/MeOH (50:50 v/v, 500 mL). The eluate was then reduced to dryness on the rotary evaporator to give the final complexes.

Band 1: $[\text{Cu}\{(\text{C}_7\text{H}_{15})_2\text{N}\}(\text{C}_7\text{H}_{15}\text{NH})\text{sar}]\text{Cl}_2 \cdot x\text{HCl}$ (0.44 g).
ESMS m/z 335.6 = $[\text{CuC}_{35}\text{N}_8\text{H}_{76}]^{2+}$; 706.8 = $[\text{CuC}_{35}\text{N}_8\text{H}_{76} + \text{Cl}]^+$.
Band 2: $[\text{Cu}(\text{C}_7\text{H}_{15}\text{NH})_2\text{sar}]\text{Cl}_2 \cdot x\text{HCl}$ (1.36 g).
ESMS m/z 286.6 = $[\text{CuC}_{28}\text{N}_8\text{H}_{62}]^{2+}$; 608.5 = $[\text{CuC}_{28}\text{N}_8\text{H}_{62} + \text{Cl}]^+$.

$[(\text{C}_7\text{H}_{15}\text{NH})_2\text{sar}] \cdot x\text{HCl}$ via reduction of $[\text{Cu}(\text{C}_7\text{H}_{15}\text{NH})_2\text{sar}] \cdot \text{Cl}_2 \cdot x\text{HCl}$ with NaBH_4 and Pd/C

Pd/C (10 % Pd, 0.21 g) was suspended in a deoxygenated 1% NaOH/MeOH solution (*ca.* 3 mL) under nitrogen, and to this was added a mixture of NaBH_4 (0.8 g, 21 mmol) in 1% NaOH/MeOH (*ca.* 5 mL). This was allowed to stir for *ca.* 5 min, at which point $[\text{Cu}(\text{C}_7\text{H}_{15}\text{NH})_2\text{sar}] \cdot \text{Cl}_2 \cdot x\text{HCl}$ (0.40 g) in 1% NaOH/MeOH (*ca.* 8 mL) was added dropwise, and the reaction mixture allowed to stir for 18 h at RT. At this point, the mixture was filtered twice through Celite, the filtrate brought to dryness on the rotary evaporator and the off-white solid obtained was extracted with Et_2O (3 x 100 mL). The Et_2O extracts were combined and the solvent removed on the rotary evaporator to give an oily white precipitate, which was dissolved in MeOH and acidified with conc. HCl until effervescence ceased. The mixture was then taken to dryness on the rotary evaporator and the white solid obtained was dissolved in MeOH and applied to a column of H^+ Dowex 50Wx2 cation exchange resin. The column was washed with H_2O (500 mL), 1 M $\text{HCl}_{(\text{aq})}$ (500 mL), MeOH (500 mL) and the ligand removed from the column with conc. HCl/MeOH (50:50 v/v, *ca.* 750 mL). The ligand solution was reduced to dryness on the rotary evaporator, and the white waxy solid redissolved in MeOH and reduced to dryness three times to give $[(\text{C}_7\text{H}_{15}\text{NH})_2\text{sar}] \cdot x\text{HCl}$ as a tacky white solid (0.29 g).

^1H NMR (CD_3OD , 500 MHz): 0.89 (t, 6H, $-\text{CH}_3$), 1.25 – 1.50 (m, 16H, tail $-\text{CH}_2-$), 1.82 (m, 4H, tail $-\text{CH}_2-$), 3.18 (m, 4H, tail $-\text{CH}_2-$), 3.4 – 3.8 (br, 24H, cage $-\text{CH}_2-$).

^{13}C NMR (CD_3OD , 125 MHz): 14.4 ($-\text{CH}_3$), 23.5, 27.55, 27.62, 29.9, 32.9, 44.0 ($-\text{CH}_2-$), 48.0, 50.6 (cage $-\text{CH}_2-$), 60.6 (C).

ESMS m/z 511.9 = $[\text{C}_{28}\text{N}_8\text{H}_{62} + \text{H}]^+$.