A Ligand Strand that Displays Anion-dependant Reactivity with Acetonitrile; Formation of either a Mononuclear Complex or Head-to-Tail Circular Helicate.

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Electronic Supplementary Information.

Chemicals were purchased and used without further purification. 1H NMR spectra were recorded on a 400 MHz Bruker Advance DP X400. Mass spectra were obtained on an Agilent 6210 TOF MS for the organic species with the metal complexes run on a Bruker MicroQTOF LC.

**Figure 1.** Synthesis of ligand L^2_2.

Synthesis of (2).

To a solution of 1,1’-biphenyl-2,2’-diamine (1) (410 mg, 2.23 mmol) in acetonitrile (50 mL) was added benzoyl isothiocyanate (794 mg, 4.90 mmol) and the reaction stirred for 3 days at RT, during
which time a colourless precipitate formed which was isolated by filtration. Washing with MeCN (3 × 5 mL) and Et₂O (3 × 5 mL) gave (2) as a white solid. Yield = 743 mg (65 %). ¹H NMR (400 MHz, DMSO-d⁶) δ (ppm) 12.2 (s, 2H, -NH), 11.4 (s, 2H, -NH), 7.86 (d, 4H, J = 7.52), 7.74 (d, 2H, J = 7.8), 7.63 (t, 2H, J = 7.4), 7.50 (t, 4H, J = 7.68), 7.43 (m, overlapping, 4H), 7.34 (t, 2H J = 7.38 Hz). ¹³C NMR [100 MHz, DMSO-d⁶]: δ (ppm) = 180.9 (C=S), 168.3 (C=O), 136.8 (Q), 135.0 (Q), 133.5 (CH), 132.5 (Q), 130.7 (CH), 129.1 (CH), 128.8 (CH), 128.7 (CH), 128.2 (CH), 127.3 (CH). ESI-MS m/z 511 (M + H⁺), HR ESI-MS found 511.1251 C₂₈H₂₂N₄O₂S₂ requires 511.1257 (error 0.93 ppm).

Figure 2. ¹H NMR of benzoylated thiourea product (2) a = water impurity and b = (CD₃)(CHD₂)SO.

Synthesis of (3)

The diurea derivative (2) (400 mg, 0.784 mmol) was suspended in water (20 mL) and NaOH (191 mg, 4.78 mmol) added. The reaction was then heated to 60°C and MeOH slowly added dropwise until all the solid dissolved (1 ~ 2 mL). After 24 hrs the solution was allowed to cool to room temperature and then immersed in an ice bath, after which time a colourless solid precipitated. Isolation by filtration and washing with ice cold water (2 x 1 mL) gave the dithiourea (3) as a colourless solid. Yield = 140 mg (59 %). ¹H NMR (400 MHz, DMSO-d⁶) δ (ppm) 8.81 (s, 2H, -NH), 7.50 (m, 4H, Ar), 7.27 (m, 4H, Ar), 7.60 – 7.0 (s, broad, overlapping, 4H, -CSNH₂). ¹³C NMR [100 MHz, DMSO-d⁶]: δ (ppm) = 183.5 (C=S), 137.0 (Q), 135.4 (Q), 131.1 (CH), 129.4 (CH), 128.5 (CH), 126.6 (CH). ESI-MS m/z 303 (M + H⁺), HR ESI-MS found 303.0732 C₁₄H₁₄N₄S₂ requires 303.0733 (error 0.41 ppm).
Synthesis of $L^{2,2}$.

The dithiourea containing compound (3) (141 mg, 0.47 mmol) was suspend in EtOH (20 mL) and to this, $\alpha$-bromoacetylpyridine hydrobromide (393 mg, 1.40 mmol) was added and the reaction heated at 80°C overnight. During this time a yellow precipitate had formed which was isolated by filtration and washed with EtOH (2 x 1 mL) and Et$_2$O (2 x 1 mL). This yellow solid was suspended in ammonia (sp. gr 0.88, 10 mL) and stirred for 24 hrs. The solid was then filtered, washed with H$_2$O (2 x 1 mL), EtOH (2 x 1 mL) and Et$_2$O (2 x 1 mL) to give $L^{2,2}$ as a cream solid. Yield = 120 mg (51 %). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 8.57 (dd, 2H, $J = 4.76$, 0.76), 8.20 (d, 2H, $J = 7.84$), 7.89 (d, 2H, $J = 7.92$ Hz), 7.70 (td, 2H, $J = 7.72$, 1.76), 7.54 (td, 2H, $J = 8.1$, 1.6 Hz), 7.33 (dd, 2H, $J = 7.56$, 1.56), 7.31 (s, 2H, tz), 7.23 (td, 2H, $J = 7.48$, 0.92), 7.18 (ddd, 2H, $J = 7.44$, 4.8, 1.0 Hz), 6.94 (2H, br s, -NH). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) = 165.6 (Q), 151.7 (Q), 149.6, 139.2 (Q), 137.6, 131.9, 130.8 (Q), 129.5 (Q), 129.0, 123.9, 122.9, 122.0, 120.8, 107.2. ESI-MS $m/z$ 505 (M + H$^+$), HR ESI-MS found 505.1256 C$_{28}$H$_{20}$N$_6$S$_2$ requires 505.1264 (error 1.24 ppm).

Figure 3. $^1$H NMR of the bis-thiourea product (3) a = water impurity and b = (CD$_3$)(CHD$_2$)SO.
Synthesis of $[\text{Cu}(L^{2,2})(\text{ClO}_4)]_2$.

To a solution of Cu(ClO$_4$)$_2$·6H$_2$O (10 mg, 0.027 mmol) in MeCN (1 ml) was added a suspension of ligand $L^{2,2}$ (13 mg, 0.026 mmol) in MeCN and the reaction warmed and sonicated until a clear light blue solution had formed. Diethyl ether was slowly allowed to diffuse into the solution resulting in blue plate-like crystals after several days. Filtration and washing with diisopropyl ether (1 ml) and diethyl ether (1 ml) gave blue crystals which lost solvent rapidly (yield = 10 mg, 51%). ESI-MS $m/z$ 666 corresponding to $\{\text{Cu}(L^{2,2})(\text{ClO}_4)\}^+$ along with higher molecular species (see text). Found: C, 42.0; H, 2.3; N, 10.2%; C$_{28}$H$_{20}$N$_6$S$_2$CuCl$_2$O$_8$·2H$_2$O requires C, 41.9; H, 3.0; N, 10.5%.

Synthesis of $[\text{Cu}_4(L^{2,3})_4](\text{trif})_8$. To a solution of Cu(triflate)$_2$ (10 mg, 0.028 mmol) in MeCN (1 ml) was added a suspension of ligand $L^{2,2}$ (14 mg, 0.026 mmol) in MeCN and the reaction warmed and sonicated until a clear light blue solution had formed. Diisopropyl ether was slowly allowed to diffuse into the solution resulting in pale blue block crystals after several days. Filtration and washing with diisopropyl ether (1 ml) and diethyl ether (1 ml) gave blue crystals which lost solvent rapidly (yield = 16 mg, 68%). ESI-MS $m/z$ 1665 corresponding to the doubly charged tetranuclear assembly (e.g. $\{[\text{Cu}_4(L^{2,3})_4](\text{trif})_6\}^{2+}$) as well as smaller fragments at $m/z$ 1261 corresponding to $\{[\text{Cu}(L^{2,2})(L^{2,3})]_2(\text{trif})\}^+$ and $m/z$ 716 ($\{[\text{Cu}(L^{2,2})(\text{trif})]\}^+$). Found: C, 41.4; H, 2.6; N, 10.0%; C$_{128}$H$_{92}$N$_{28}$S$_{16}$Cu$_4$F$_{24}$O$_{24}$·2H$_2$O requires C, 41.9; H, 2.6; N, 10.7%.
**Figure 5.** ESI-MS of the reaction of Cu(ClO$_4$)$_2$ and L$^{2-2}$ (sample time 10 minutes).
Figure 6. ESI-MS of the reaction of Cu(ClO$_4$)$_2$ and L$_{2,2}$ (sample time 10 minutes) showing the isotope pattern (observed top and calculated bottom) for the ions at a) m/z 666 corresponding to {[Cu(L$_{2,2}$)](ClO$_4$)}$^+$, b) m/z 1433 corresponding to {[Cu$_2$(L$_{2,2}$)$_2$](ClO$_4$)$_3$}$^+$ and c) m/z 2201 corresponding to {[Cu$_3$(L$_{2,2}$)$_3$](ClO$_4$)$_5$}$^+$. 
Figure 7. ESI-MS of the reaction of Cu(ClO$_4$)$_2$ and L$^{2-2}$ (sample time 6 days).
Figure 8. ESI-MS of the reaction of Cu(triflate)$_2$ and L$_{2,2}$ (sample time 10 minutes).

Figure 9. ESI-MS of the reaction of Cu(trif)$_2$ and L$_{2,2}$ (sample time 10 minutes) showing the isotope pattern (observed top and calculated bottom) for the ion at $m/z$ 716 corresponding to $\{[\text{Cu}(L_{2,2})(\text{trif})]\}^\pm$. 
Figure 10. ESI-MS of the reaction of Cu(trif)$_2$ and L$^{2,2}$ (sample time 6 days).
Figure 11. ESI-MS of the reaction of Cu(triflate)$_2$ and L$^{2-}$ (sample time 6 days) showing the isotope pattern (observed top and calculated bottom) for the ion at a) m/z 716 corresponding to $\{\text{Cu(L}^{2+})\text{(trif)}\}^+$, b) m/z 757 corresponding to $\{\text{Cu(L}^{3+})\text{(trif)}\}^+$, c) m/z 1261 corresponding to $\{\text{Cu(L}^{2+})\text{(L}^{2+})\text{(trif)}\}^+$ and d) m/z 1665 corresponding to $\{\text{Cu}_n\text{(L}^{2+})_4\text{(trif)}_n\}^{2+}$. 
Figure 12. ESI-MS of the reaction of Cu(ClO$_4$)$_2$ and L$_{2,2}$ in 10% MeOH in MeCN (sample time 6 days).

Figure 13. ESI-MS of the reaction of Cu(ClO$_4$)$_2$ and L$_{2,2}$ in 10% MeOH in MeCN (sample time 6 days) showing the isotope pattern (observed top and calculated bottom) for the ion at a) $m/z$ 707 corresponding to $\{[\text{Cu}(L^{2,3})](\text{ClO}_4)\}^+$ and b) $m/z$ 1517 corresponding to $\{[\text{Cu}_4(L^{2,3})_4](\text{ClO}_4)_3\}^{2+}$. 
Figure 14. ESI-MS of the reaction of Cu(trif)$_2$ and L$_{2,2}$ in 10% MeOH in MeCN (sample time 6 days).
Figure 15. ESI-MS of the reaction of Cu(BF$_4$)$_2$ and L$_{12}$. 
**Figure 16.** ESI-MS of the reaction of Cu(BF₄)₂ and L²⁻ showing the isotope pattern for the ion at m/z 1396 corresponding to both the singly charged \{[Cu₂(L²⁻)₂][BF₄]₃\}⁺ ion (middle) and the doubly charged \{[Cu₄(L²⁻)₄][BF₄]₆\}²⁺ ion (bottom).

**Crystallography.**

Single crystal X-ray diffraction data was collected at 150(2) K on a Bruker D8 Venture diffractometer equipped with a graphite monochromated Mo(Kα) radiation source and a cold stream of N₂ gas. Solutions were generated by conventional heavy atom Patterson or direct methods and refined by full-matrix least squares on all F² data, using SHELXS-97 and SHELXL software respectively.¹ Absorption corrections were applied based on multiple and symmetry-equivalent measurements using SADABS.²

Crystal for [Cu(L²⁻)](ClO₄)₂. Crystal data for C₃₀H₂₃Cl₂CuN₇O₈S₂, M = 808.11, monoclinic, a = 11.3506 (6) Å, b = 40.5564 (19) Å, c = 7.2871 (3) Å, β = 106.1473 (16)°, V = 3222.2 (3) Å³, T = 150 K, space group P2₁/c, Z = 4, 36819 independent reflections measured, 9399 independent reflections (Rint = 0.0639). The final R₁ values were 0.0698 (I > 2σ(I)). The final wR(F²) values were 0.1260 (I > 2σ(I)). The final R₁ values were 0.1180 (all data). The final wR(F²) = 0.1405 (all data). The goodness of fit on F² was 1.101. CCDC 1574886. The structure contained a rotationally disordered perchlorate counter ion and it was modelled in two positions using the PART instruction. For the three disordered atoms SIMU, SADI and ISOR constrains were used in the least-squares refinement.

Crystal for [Cu₄(L²⁻)₄](trif)₈. Crystal data for C₁₃₆H₁₀₄Cu₄F₂₄N₃₂O₂₅S₁₆, M = 3809.77, monoclinic, a = 40.4596 (19) Å, b = 17.1105 (8) Å, c = 23.5882 (12) Å, β = 95.1214 (18)°, V = 16264.5 (14) Å³, T = 150 K, space group C2/c, Z = 4, 80137 reflections measured, 24779 independent reflections (Rint = 0.0531). The final R₁ values were 0.0753 (I > 2σ(I)). The final wR(F²) values were 0.1820 (I > 2σ(I)). The final R₁ values were 0.1297 (all data). The final wR(F²) = 0.2180 (all data). The goodness of fit on F² was 1.0765. CCDC 1574887. The structure contained a acetonitrile and a water molecule disordered over two sites and they were modelled in two positions using the PART instruction with SIMU, SADI and ISOR constrains used in the least-squares refinement. Furthermore, the structure contained disorder that could not be satisfactorily modelled and as a result the diffuse electron density was removed using the solvent mask facility in Olex2, resulting in voids in the crystal structure.³ The solvent mask removed a total of 133.1 electrons in the unit cell which corresponds to six molecules of acetonitrile in the unit cell.


². G. M. Sheldrick, SADABS: A Program for Absorption Correction with the Siemens SMART System, University of Göttingen (Germany), 1996.