

A Non-Platonic M_4L_4 Complex Constructed Using Heterotopic Ligands

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Supporting Information

Crystallographic Details

Data for $[Cu_4Cl_2(L^2)_4] \cdot 2ClO_4$ (**1**) and $[Cu(L^2H)_2] \cdot 2ClO_4 \cdot 2H_2O$ (**2**) were collected using the MX1 beamline at the Australian Synchrotron, Victoria, Australia. The wavelength was set at 0.7107 Å (17.4 keV) and data collection temperatures were maintained at 100 K using an open-flow N_2 cryostream. Data collection was conducted using the BluIce package.^[1] Indexing and integration was conducted using the program XDS.^[2]

Structures were solved by direct methods using SHELXS^[3] and were refined by alternating least-squares cycles using SHELXL^[3] with X-Seed as a graphical interface.^[4] All non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms attached to carbon were placed in idealised positions and refined using a riding model in both structures. Refinement details specific to each structure are given below.

Crystal data for $[Cu_4(L^2)_4Cl_2] \cdot 2(ClO_4)$ (1**):** $C_{76}H_{60}Cl_4Cu_4N_{16}O_{20}$, $M = 1913.36$, yellow block, 0.10 x 0.10 x 0.08 mm³, monoclinic, space group $P2_1/c$ (No. 14), $a = 18.273(4)$, $b = 43.561(9)$, $c = 22.573(5)$ Å, $\beta = 103.17(3)^\circ$, $V = 17495(6)$ Å³, $Z = 8$, $D_c = 1.453$ g/cm³, $F_{000} = 7776$, $2\theta_{max} = 57.2^\circ$, 303280 reflections collected, 40546 unique ($R_{int} = 0.0532$). Final $GooF = 1.032$, $RI = 0.0751$, $wR2 = 0.2061$, R indices based on 33419 reflections with $I > 2\sigma(I)$ (refinement on F^2), 2314 parameters, 113 restraints, $\mu = 1.157$ mm⁻¹.

The perchlorate counter-anions are disordered in the structure of **1**. The four anions within the asymmetric unit have been modelled across five sites with partial occupancy (of which two sites have been refined with further disorder around a central position). Due to the low occupancy and disorder, distance restraints have been used for Cl-O and O...O distances in many instances. Anisotropic displacement parameters are slightly enlarged for the counter-anions, as is expected for such disordered species. One methoxy group of an L2 ligand is also disordered and has been refined with a 50:50 occupancy model and C-O distance restraints.

The structure contains void space with residual electron density above the noise level which could not be assigned to any molecular fragments and appears to be lattice solvent. The fully refined structure was treated using the SQUEEZE routine in PLATON.^[5] A total void volume of 2162 Å³ per unit cell was located (12 %) with 472 e⁻. Microanalyses on a fully

dried sample suggest that the void space contains only volatile species (likely MeCN, MeOH and H₂O from the synthesis). The complexes pack in one-dimensional chains parallel to the *a*-axis with the largest voids being between these chains (Figure S1).

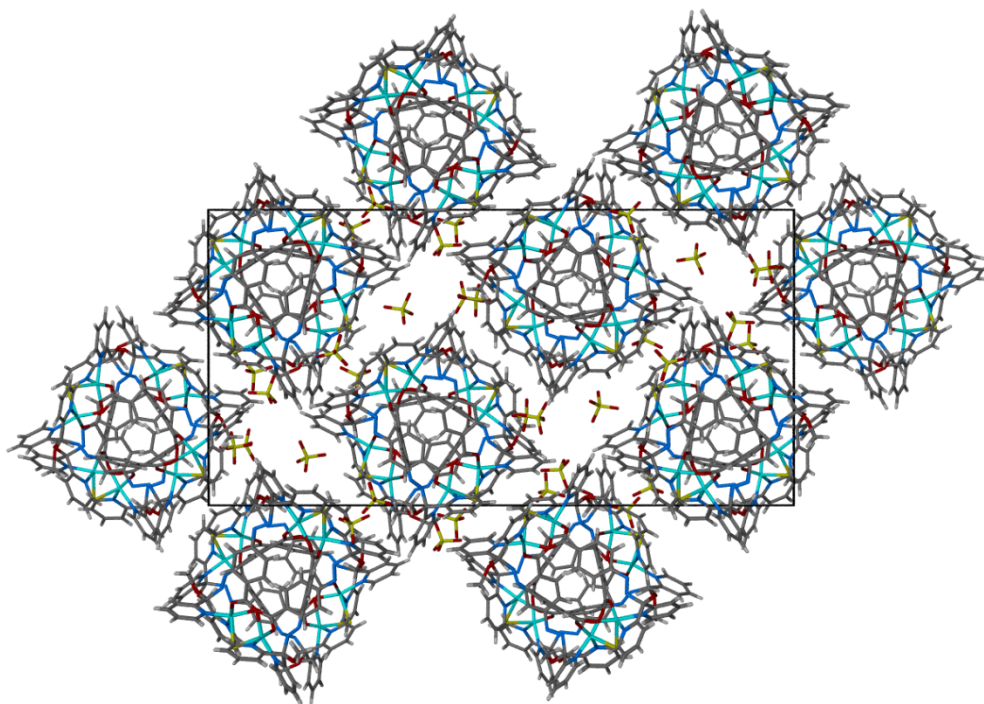


Figure S1: Crystal packing in the structure of **1**, viewed along the *a*-axis.

Crystal data for [Cu(L²H)₂]₂·2(ClO₄)·2H₂O (2**):** C₃₈H₃₆Cl₂CuN₈O₁₆, *M* = 995.19, yellow block, 0.04 x 0.04 x 0.02 mm³, monoclinic, space group *P*2₁/*c* (No. 14), *a* = 11.707(2), *b* = 15.548(3), *c* = 12.323(3) Å, β = 115.34(3)°, *V* = 2027.3(7) Å³, *Z* = 2, *D_c* = 1.630 g/cm³, *F*₀₀₀ = 1022, 2θ_{max} = 61.6°, 43145 reflections collected, 6297 unique (*R*_{int} = 0.1035). Final *GooF* = 1.058, *R*1 = 0.0624, *wR*2 = 0.1828, *R* indices based on 4954 reflections with *I* > 2σ(*I*) (refinement on *F*²), 317 parameters, 4 restraints, μ = 0.757 mm⁻¹.

Hydrogen atoms attached to oxygen in **2** were located from the Fourier difference map and refined with a restrained O-H distance of 0.84 Å. The hydrogen atoms of the water molecule were also refined using a non-bonding distance restraint.

X-Ray Powder Diffraction

X-ray powder data were collected at room temperature using a Bruker D8 Focus instrument equipped with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) at room temperature. Simulated patterns were calculated from the low temperature single-crystal data using the program Lazy Pulverix.^[6]

It is evident from comparing the experiment plots with the calculated patterns that both compounds **1** and **2** are present as crystalline products regardless whether a Cu(I) or Cu(II) precursor is used (Figure S2).

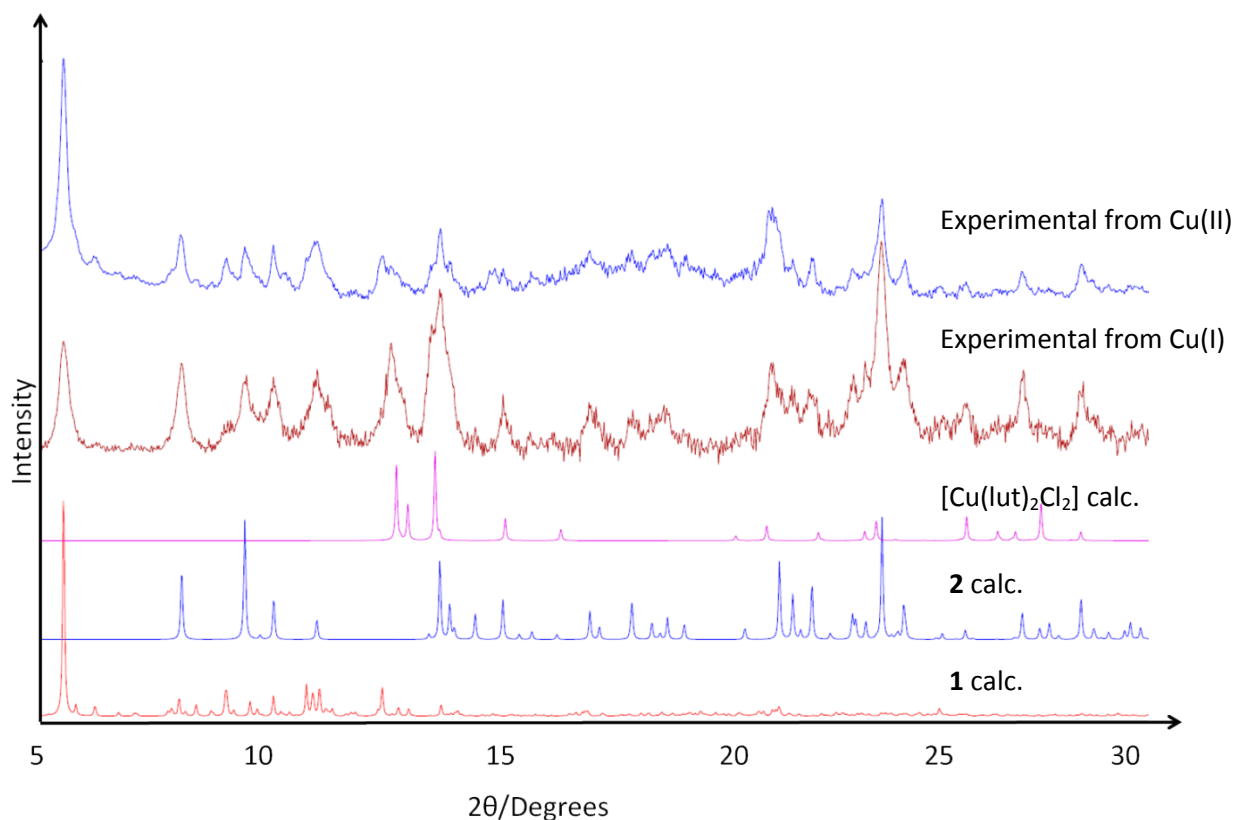


Figure S2: Comparison of room temperature experimental powder X-ray diffraction patterns for the synthesis of **1** and **2** from Cu(I) and Cu(II) precursors with the calculated patterns of the two compounds (derived from low temperature single-crystal experiments) and [Cu(2,6-lutidine)₂Cl₂]. Compounds **1** and **2** are observed in both experimental patterns.

Mass Spectrometry

Data were collected using a Bruker maXis instrument in positive ESI mode at the University of Canterbury, New Zealand (Figure S3). The major peak at $m/z \sim 759$ corresponds to the [Cu(L₂H)₂]⁺ species (Figure S4). The tetrahedral complex is observed as a 2+ ion at $m/z \sim$

820 (Figure S5). Signals are also observed for $[\text{Cu}(\text{L}_2\text{H})_2]^{2+}$ ($m/z = 379$), $[\text{Cu}(\text{L}^2)]^+$ ($m/z = 411$) and an overlapping signal for $[\text{Cu}(\text{L}^2)\text{Cl}]^+$ ($m/z = 446$) and $[\text{Cu}(\text{L}^2)(\text{MeCN})]^+$ ($m/z = 452$). There is no evidence of solvent inclusion within the tetrahedral complex.

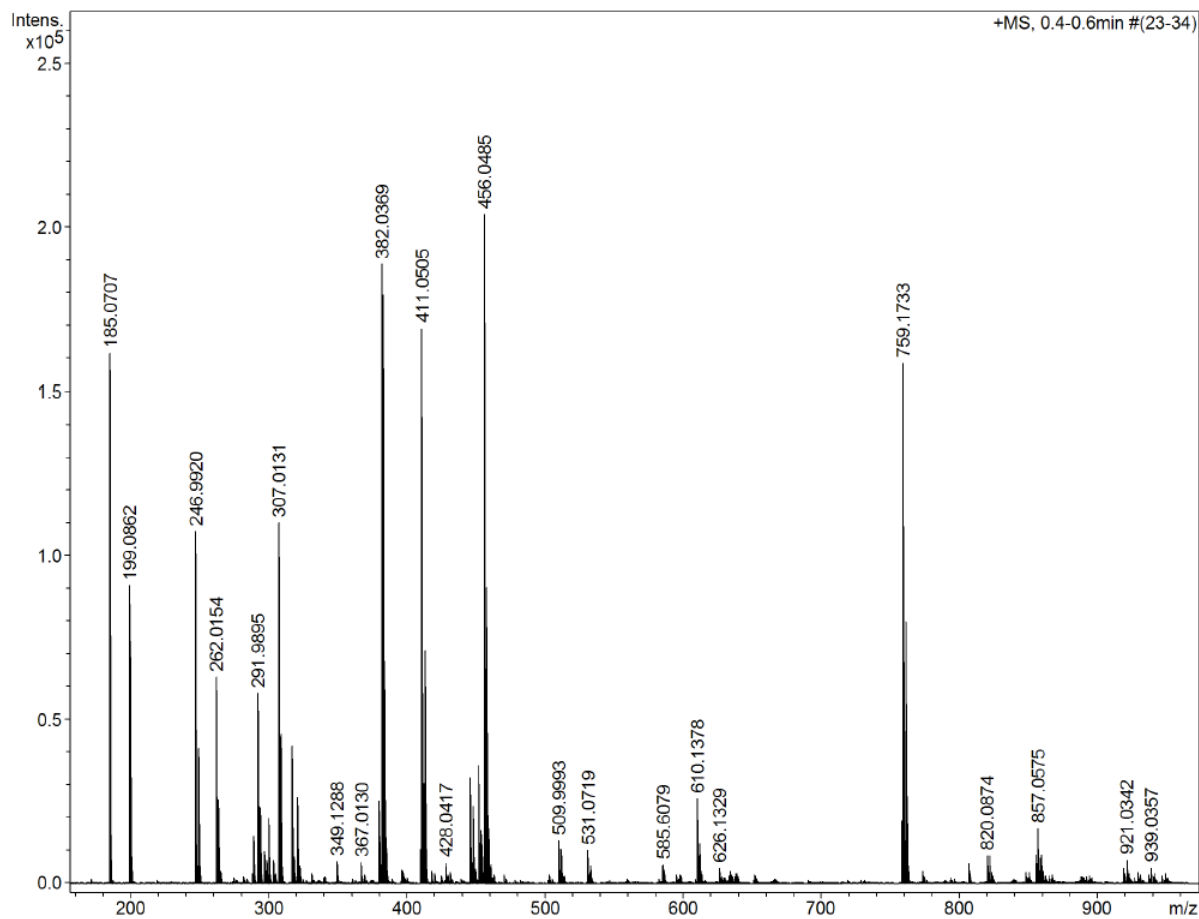


Figure S3: Full mass spectrum of a sample of 1 and 2 (prepared from Cu(II) precursor) dissolved in acetonitrile.

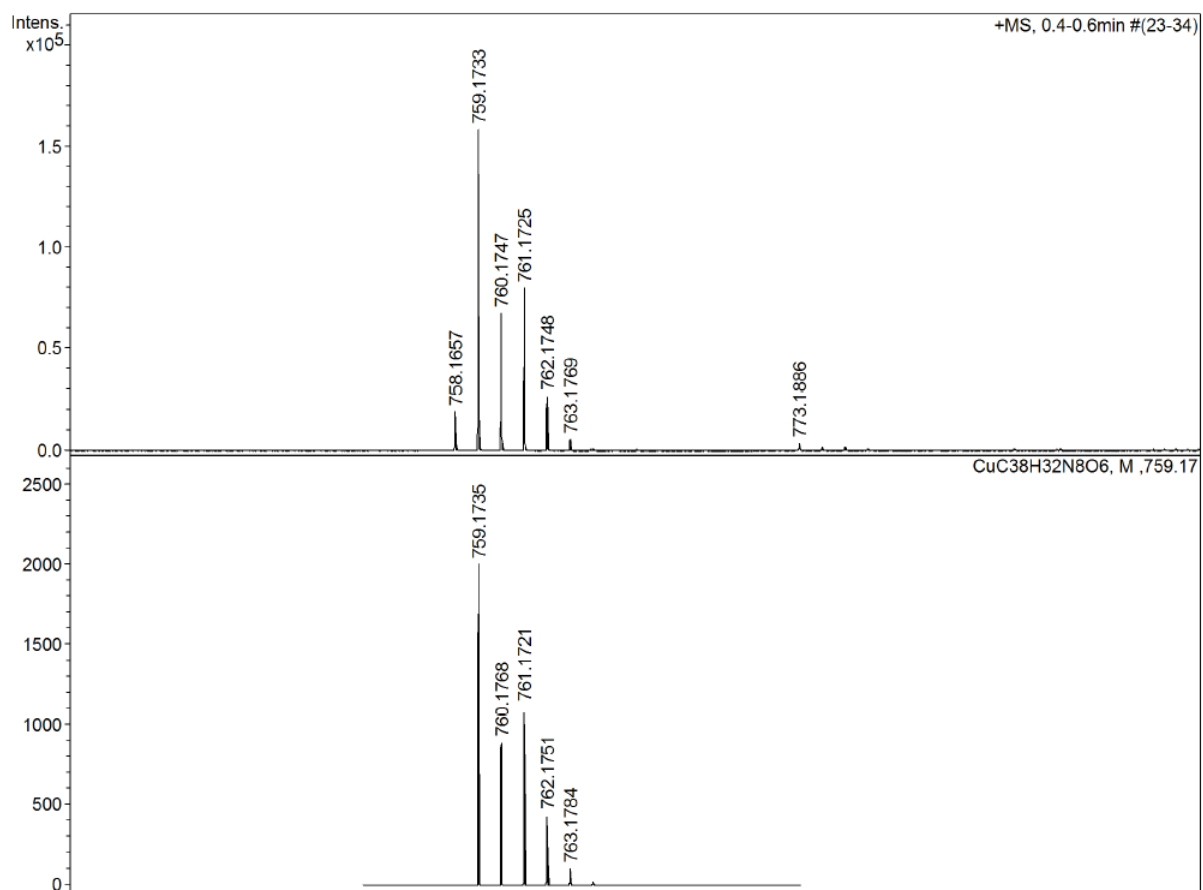


Figure S4: Comparison of the experimental mass spectra (top) with the calculated isotope pattern (bottom) for $m/z \sim 759$ corresponding to $[\text{Cu}(\text{L}^2\text{H})_2]^+$.

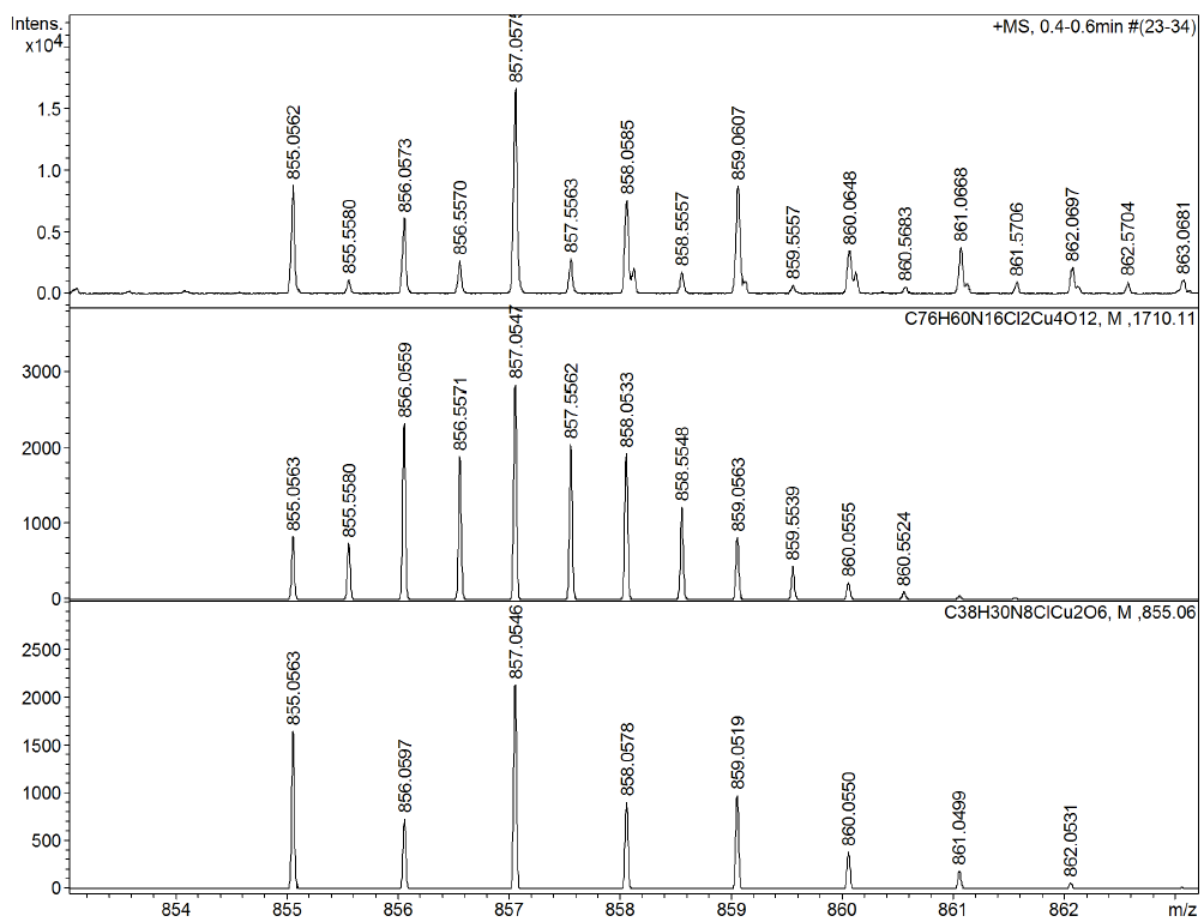


Figure S5: Comparison of the experimental mass spectra for $m/z \sim 857$ (top) with the calculated isotope patterns corresponding to $[\text{Cu}_4(\text{L}^2)_4\text{Cl}_2]^{2+}$ (middle) and $[\text{Cu}_2(\text{L}^2)_2\text{Cl}]^+$ (bottom).

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