

Supporting Information

Saddling up Copper – New Twists on a Metallo-wheel

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Contents

S2 Experimental details.....	2
S3 Synthesis.....	3
S4 NMR Spectra of L.....	4
S5 UV-Vis and EPR spectra	5
S6 Magnetic Data	6
S7 X-ray Crystallography	8
S8 References.....	10

S2 Experimental details

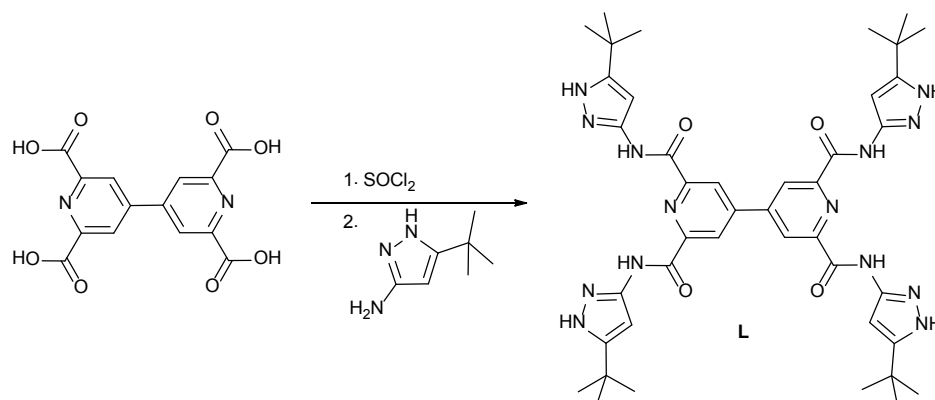
General Considerations

All experiments were performed under a nitrogen atmosphere unless stated otherwise. Dry solvents were obtained from a Puresolve PS MD-4 solvent purification system. [4,4'-Bipyridine]-2,2',6,6'-tetracarboxylic acid was synthesized following the method described previously.¹ All other chemicals were commercially available and used as received, unless otherwise stated.

Physical Measurements.

NMR spectra were recorded on a Bruker Avance AV 600 Digital NMR spectrometer with a 14.1 Tesla Ultrashield Plus magnet and chemical shifts determined with reference to residual solvent. Samples for FT-IR were pressed as KBr pellets and their spectra were recorded using a Bomem MB-100 spectrometer. Fast Atom Bombardment (FAB) mass spectra were obtained using a Kratos Concept 1S High Resolution E/B mass spectrometer. Samples for elemental analysis were submitted to Atlantic Microlab, Norcross, GA. Melting points were obtained on a Stuart Scientific SMP 10 apparatus. Electron Paramagnetic Resonance (EPR) data of **1** were recorded as a frozen MeOH solution in quartz tubes on a Bruker CW X-band (9 GHz) spectrometer equipped with a liquid N₂ cryostat; simulations were undertaken using PIP (M. Nilges, Illinois EPR Research Centre) *via* a Windows interface (PIP for Windows v1.2, J. M. Rawson, University of Windsor, 2011). Magnetic susceptibility measurements were obtained using a Quantum Design MPMS SQUID magnetometer in an applied field of 5000 G between 5 and 300 K.

S3 Synthesis



*N*2,*N*2',*N*6,*N*6'-tetrakis(5-(*tert*-butyl)-1*H*-pyrazol-3-yl)-[4,4'-bipyridine]-2,2',6,6'-tetracarboxamide, **L**

A mixture of [4,4'-bipyridine]-2,2',6,6'-tetracarboxylic acid (2.80 g, 8.43 mmol) and SOCl_2 (15 mL) were refluxed for 5 h under N_2 . The SOCl_2 was then removed under reduced pressure and the resulting tetracarbonyl chloride cooled in an ice bath for 15 min. Dry toluene (30 mL) and 3-amino-5-*tert*-butylpyrazole (4.7 g, 33.72 mmol) were then added and the reaction refluxed overnight. The solvent was removed under reduced pressure and the resulting pale yellow solid dissolved in DCM and neutralised with 5% aqueous NaHCO_3 . The organic layer was collected, washed with water and dried over Na_2SO_4 . Removal of the solvent afforded the crude product which was washed with EtOH to afford the desired ligand as a pale yellow solid. Yield: 4.53 g (66%). Single crystals suitable for X-ray diffraction were grown via diffusion of Et_2O into a DMF solution at room temperature.

^1H NMR (500 MHz, d_6 -DMSO): $\delta_{\text{H}} = 12.36$ (4H, s, pyrazole NH), 11.83 (4H, s, amide NH), 8.70 (4H, s, *m*-py CH), 6.58 (4H, s, pyrazole CH), 1.33 (36H, s, $12 \times \text{CH}_3$); ^{13}C NMR (150 MHz, d_6 -DMSO) 161.5, 153.0, 150.8, 147.5, 146.7, 123.1, 94.8, 31.2, 30.4. HRMS (FAB) $m/z = 817.43742$, $[\text{M}]^+$; calc'd for $\text{C}_{42}\text{H}_{52}\text{N}_{14}\text{O}_4 = 817.43295$.

Elemental Analysis: found C 56.91%, H 6.65%, N 20.86%, calc'd for $\text{C}_{42}\text{H}_{52}\text{N}_{14}\text{O}_4 \cdot 3.3\text{H}_2\text{O} \cdot \text{EtOH}$ C 57.29%, H 7.06%, N 21.26%. IR (KBr, cm^{-1}) $\tilde{\nu} = 3339$ (sh), 3175(br), 1689(sh), 1541(sh); Mpt > 300 °C

$[\text{Cu}_8\text{L}_4\text{Cl}_{16}] \cdot \text{CHCl}_3 \cdot 7\text{MeOH} \cdot 5\text{H}_2\text{O}$, (**1**)

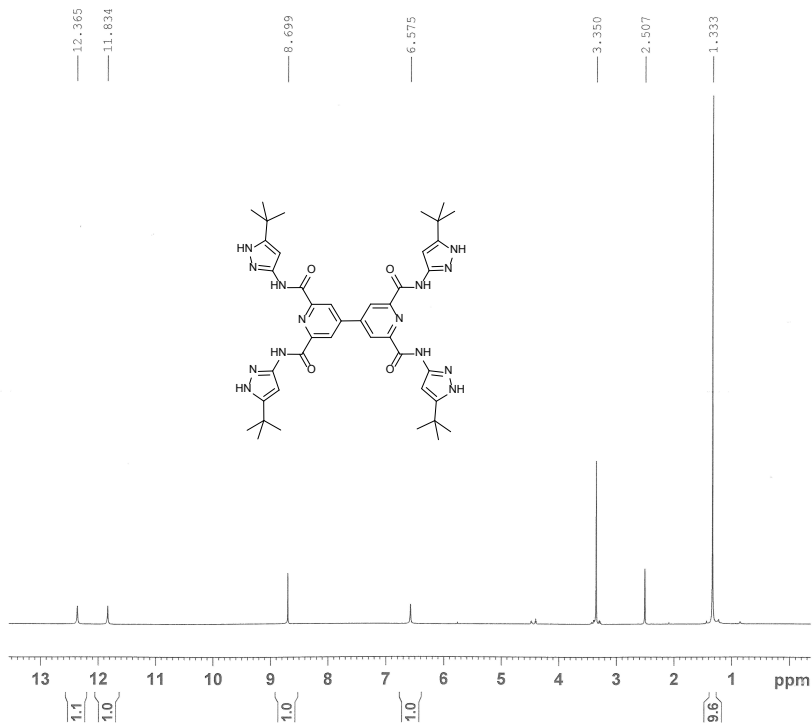
Carboxamide ligand **L** (400 mg, 0.49 mmol) was dissolved in CHCl_3 (15 mL) and a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (167 mg, 0.98 mmol) in MeOH (5 mL) was carefully layered over the top of the solution. Green plates suitable for X-ray diffraction were obtained after 2 weeks. Yield: 486 mg (21%).

MS (FAB) $m/z = 1089$ $[\text{Cu}_3\text{LCl} + \text{H}_2\text{O} + \text{MeOH}]^+$ 5%, 977 $[\text{Cu}_2(\text{L}-2\text{H})\text{Cl}]^+$ 10%, 942 $[\text{Cu}_2\text{L}]^+$ 35%, 879 $[\text{CuL}]^+$ 100%. Elemental Analysis: found C 44.29%, H 5.11%, N 16.44%, calc'd for $[\text{Cu}_8\text{L}_4\text{Cl}_{16}] \cdot \text{CHCl}_3 \cdot 5\text{H}_2\text{O} \cdot 7\text{MeOH}$ C 44.25%, H 5.21%, N 16.42%. FT-IR (KBr, cm^{-1}) $\tilde{\nu} = 3329$ (sh), 1694(sh), 1640(sh), 1574(sh), 1548(sh). UV-Vis (MeOH, nm) $\lambda_{\text{max}} = 261$ ($\epsilon = 81048 \text{ M}^{-1} \cdot \text{cm}^{-1}$), 797 ($\epsilon = 854 \text{ M}^{-1} \cdot \text{cm}^{-1}$). EPR (100 K) $g_x = 2.224$, $g_y = 2.065$, $g_z = 2.035$.

The low yields in this reaction reflect to a large extent the insolubility of the carboxamide ligand **L** in organic solvents. Attempts were made to increase the solubility of the ligand by introducing *t*-butyl groups onto the framework of the pyrazole rings. Evaporation of the filtrate from the above reaction afforded a green solid that contained a mixture of Cu(II) species and unreacted ligand which proved impossible to separate. Attempts to modify the reaction conditions afforded powders rather than single crystals which proved difficult to purify and characterize.

S4 NMR Spectra of L

1d proton

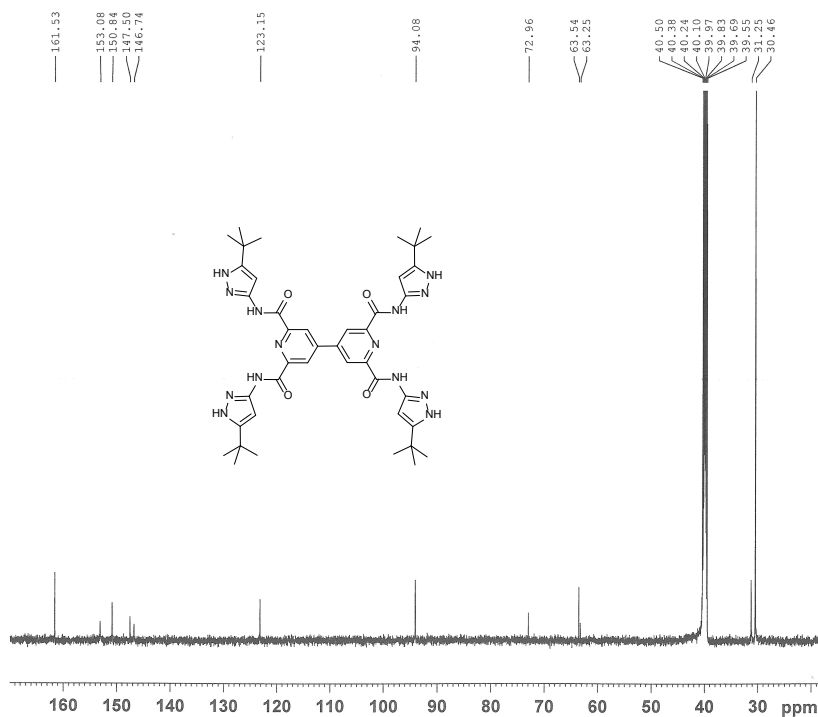


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PROCNO    1
Date_     20080925
Time      11.13
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PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         32768
SOLVENT   DMSO
NS         4
DS         0
SWH        12376.237 Hz
FIDRES     0.377693 Hz
AQ         1.3239176 sec
RG         161
DW         40.400 usec
DE         6.00 usec
TE         295.0 K
D1         1.00000000 sec
TD0        1

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NUC1      1H
P1         11.00 usec
PL1        -4.00 dB
PL1W       31.54786682 W
SFO1       600.2037065 MHz
SI         32768
SF         600.2000000 MHz
WDM        EM
SSB         0
LB         0.30 Hz
GB         0
PC         1.00
    
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1d carbon with proton decoupling



```

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PROCNO    1
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PULPROG   zgpg30
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SOLVENT   DMSO
NS         1024
DS         0
SWH        35971.223 Hz
FIDRES     1.097755 Hz
AQ         0.4555391 sec
RG         11585.2
DW         13.900 usec
DE         6.00 usec
TE         295.4 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1

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PL1        -1.00 dB
PL1W       92.33850861 W
SFO1       150.9355021 MHz

===== CHANNEL f2 =====
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PCPD2     70.00 usec
PL2        -4.00 dB
PL12       12.07 dB
PL13       15.00 dB
PL2W       31.54786682 W
PL12W     0.77977633 W
PL13W     0.39716411 W
SFO2       600.2024008 MHz
SI         32768
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WDM        EM
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LB         1.00 Hz
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PC         1.40
    
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S5 UV-Vis and EPR spectra

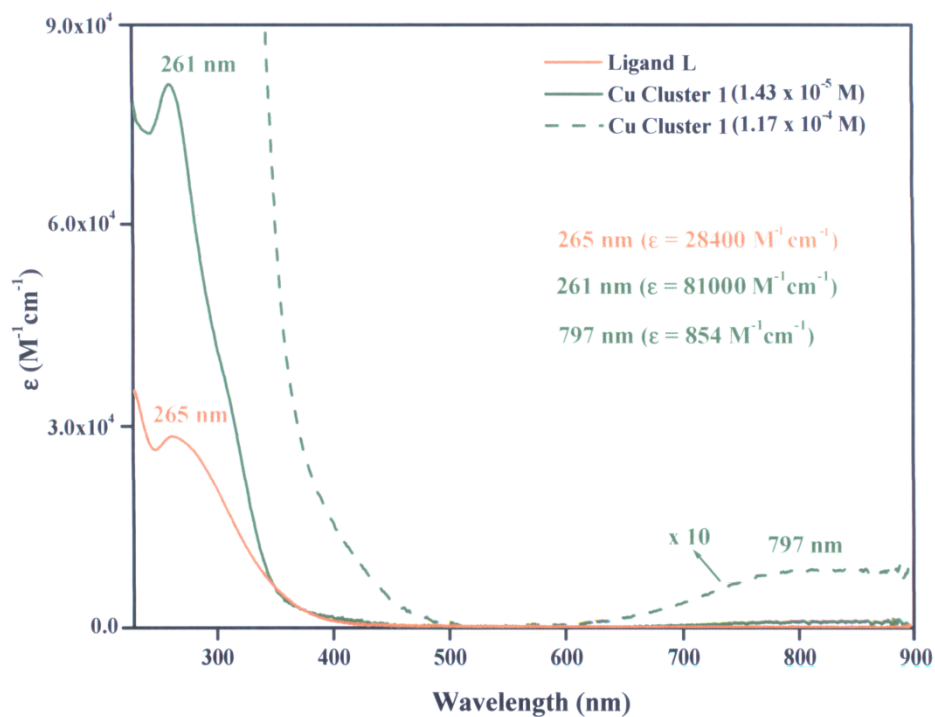


Figure 1 UV-Vis absorption spectra of complex **1** and the corresponding ligand **L** in DCM/MeOH (3:1) at room temperature

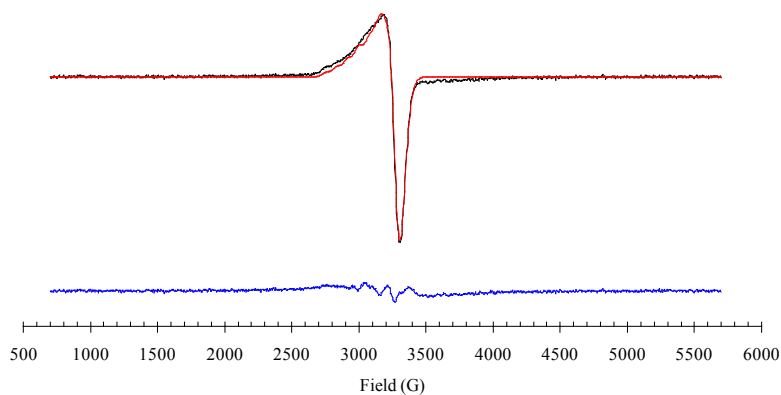


Figure 2 Frozen EPR spectrum of **1** in MeOH (black = experimental; red = simulation; blue = difference). Simulation parameters: $g_1 = 2.224$, $g_2 = 2.065$ and $g_3 = 2.035$; $a_{Cu1} = 80$ G, $a_{Cu2} = a_{Cu3} = 0$. Line width (Gaussian) $\Delta H_{pp1} = 47$ G, $\Delta H_{pp2} = 20$ G, $\Delta H_{pp3} = 20$ G.

S6 Magnetic Data

The magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 and 300 K for dc-applied fields ranging from -7 to +7 T. Dc analyses were performed on polycrystalline sample of 13.5 mg, wrapped in a polyethylenemembrane and under a field ranging from 0 to 7 T between 1.8 and 300 K. A diamagnetic correction was applied for the sample holder.

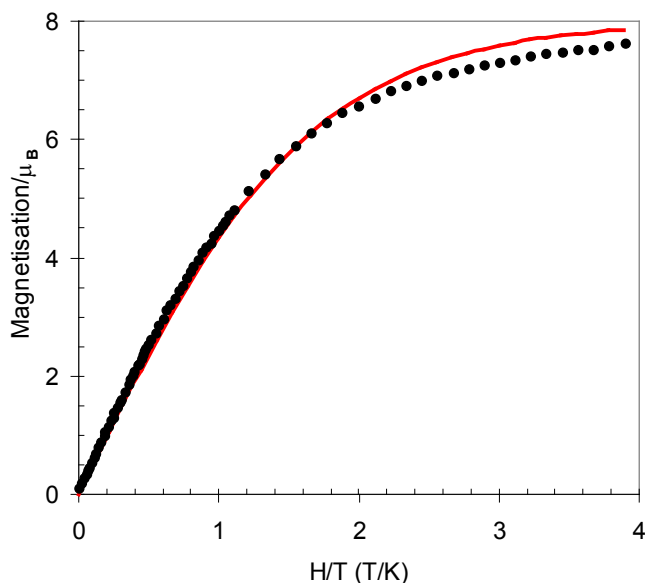


Figure 3. Field dependence of the magnetization of **1** at 1.8 K. Red line represents a fit to the Brillouin function for $8 \times S = \frac{1}{2}$ with $g = 2.108$, consistent with negligible communication between $S = \frac{1}{2}$ Cu^{II} centres.

The magnetism of **1** follows Curie-Weiss behaviour down to base temperature (1.8 K) with $C = 3.59 \text{ emu.K.mol}^{-1}$ and $\theta = -0.74 \text{ K}$, also consistent with eight independent $S = \frac{1}{2}$ ions with $g = 2.1$ exhibiting weak antiferromagnetic interactions. The small value for the Weiss constant is consistent with the absence of strong super-exchange interactions within the core of **1** and is likely due to through space dipole-dipole interactions which may be inter- or intra-molecular in nature and decay as $1/r^3$. Since the $\text{Cu}\cdots\text{Cu}$ distances around the rim ($7.462(1) \text{ \AA} - 8.695(1) \text{ \AA}$) are considerably shorter than (i) the intra-molecular trans-apical contacts ($13.818(1) \text{ \AA}$ and $13.135(1) \text{ \AA}$) and (ii) the closest inter-cluster $\text{Cu}\cdots\text{Cu}$ contacts (shortest at $10.324(1) \text{ \AA}$), then the simplest model would be a symmetric octanuclear ring of the form:

$$\hat{H} = -2J \cdot \sum_{i=1}^7 \hat{S}_i \hat{S}_{i+1} - 2J \hat{S}_8 \hat{S}_1 \quad \text{Eq. 1}$$

where only the closest $\text{Cu}\cdots\text{Cu}$ contacts contribute to the magnetism. Such large rings approximate closely to the chain model (Eq. 2) and we therefore fitted the magnetism to a copper chain with nearest-neighbour antiferromagnetic exchange with the data scaled by a factor of 8 to be commensurate with the octanuclear nature of the cage.²

$$\hat{H} = -2J \cdot \sum \hat{S}_i \hat{S}_{i+1} \quad \text{Eq. 2}$$

A fit of the data to the Bonner-Fisher model (Eq. 3) afforded $g = 2.194$ and $J/k = -0.68$ K consistent with the absence of significant super-exchange pathways (Fig. 4).

$$\chi = \frac{Ng^2\beta^2}{kT} \frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3} \quad \text{where } x = J/kT \text{ and } A = 0.25, B = 0.14995, C = 0.30094$$
$$D = 1.9862, E = 0.68854 \text{ and } F = 6.0626$$

Eq. 3

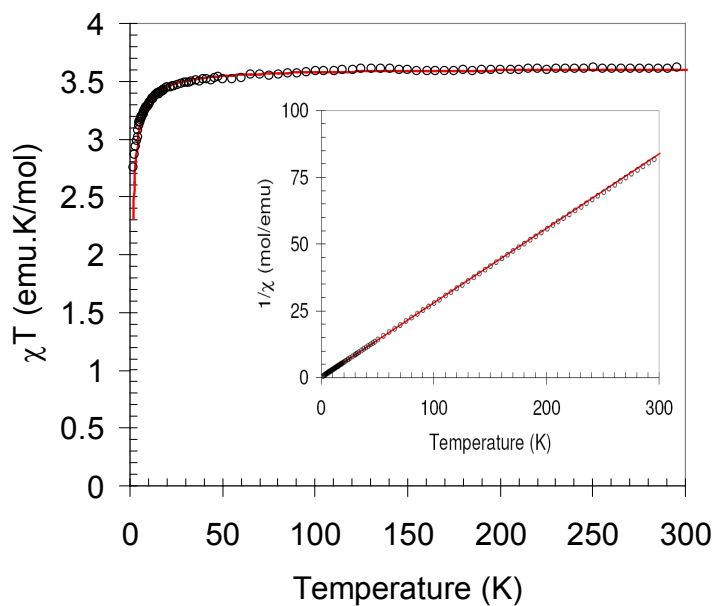


Figure 4. Plot of χT vs T for **1** (solid red-line represents the fit to the antiferromagnetic chain model of Bonner and Fisher); inset: Curie-Weiss behaviour of **1**.

S7 X-ray Crystallography

Single crystals of ligand **L** and complex **1** were mounted on a cryoloop with paratone oil and examined on a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryoflex low temperature device. Data were measured at 150(2) K using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) and the APEX-II software.³ Final cell constants were determined from full least squares refinement of all observed reflections. The data were corrected for absorption (SADABS).⁴ For both compounds, the structures were solved by direct methods and refined with full least squares refinement on F^2 within the SHELXTL suite.⁵ Hydrogen atoms were placed at calculated positions and refined isotropically with a riding model using SHELXTL default parameters. For cluster **1**, there was disorder in the *tert*-butyl groups, the majority of which were split into two components. One CHCl₃ molecule was refined satisfactorily split into two components. From the remaining electron density a second CHCl₃ molecule could be identified with partial occupancy together with six methanol molecules and an uncertain number of water molecules. All attempts to refine this solvent were less than acceptable. As a consequence, the disordered solvent was removed from the model using the PLATON/SQUEEZE.⁶ About 30% of the total volume of the cluster is solvent accessible space. The cif file includes only the chemical formula of the cluster itself and not the solvent, which accounts for the alerts in PLATON.

Table 1. X-ray crystallographic information for **L** and cluster **1**

Compound reference	L	1
Chemical formula	C ₂₂ H ₁₆ N ₆	C ₁₆₈ H ₂₀₈ Cl ₁₆ Cu ₈ N ₅₆ O ₁₆
Formula Mass	364.41	4343.42
Crystal system	monoclinic	triclinic
<i>a</i> /Å	10.9614(6)	21.5918(15) Å
<i>b</i> /Å	20.1743(11)	24.0051(17) Å
<i>c</i> /Å	8.7356(5)	27.3864(19) Å
α /°	90.00	83.750(4)°
β /°	101.490(3)	85.664(4)°
γ /°	90.00	69.107(3)°
Unit cell volume/Å ³	1893.06(18)	13172.2(16) Å ³
Temperature/K	150(2)	150(2)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
No. of formula units per unit cell, <i>Z</i>	4	2
No. of reflections measured	29931	175202
No. of independent reflections	4286	42801
<i>R</i> _{int}	0.0466	0.0475
Final <i>R</i> _{<i>I</i>} values (<i>I</i> > 2σ(<i>I</i>))	0.0529	0.0749
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.0994	0.2084
Final <i>R</i> _{<i>I</i>} values (all data)	0.0869	0.1050
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.1110	0.2277

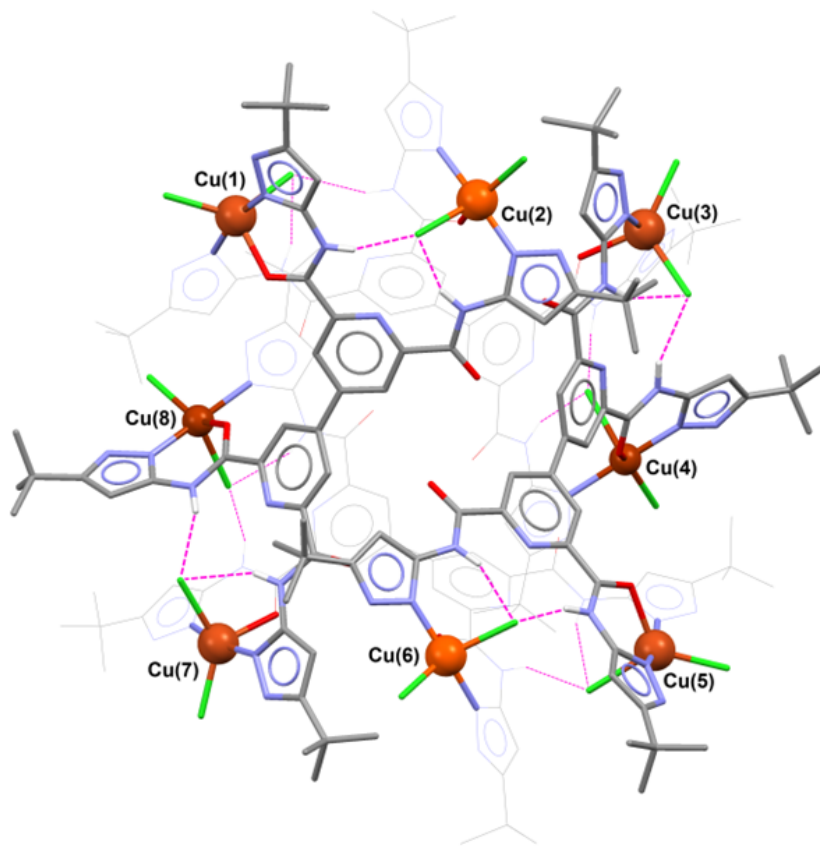


Figure 5. View of the octanuclear cluster $[\text{Cu}_8\text{L}_4\text{Cl}_{16}]$ **1** along its approximate S_4 axis with the top surface ligands highlighting the hydrogen bonding interactions between amide NH and chloride ligands. (pink dashed lines).

S8 References

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