Supplementary data for *Dalton Transactions*

A Novel $[Cu^{II}_4]$ Cluster From the Assembly of Two $[Cu^{II}_2L]^+$ Units by a Central $\mu_4-\eta^2:\eta^2$ Perchlorate Ligand

Alok Ranjan Paital,[a] Valerio Bertolasi,[d] Guillem Aromí,*[,b] Jordi Ribas-Ariño[c] and Debashis Ray*[,a]

[a] *Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India. Fax: 03222-25530; Tel: 03222-283324; E-mail: dray@iitkgp.ernet.in*

[b] *Departament de Química Inorgànica, Universitat de Barcelona, 08028 Barcelona, Spain. Fax: +34 93 4907725; Tel: +34 93 4039760; E-mail: guillem.aromi@qi.ub.es*

[c] *Departament de Química Física and CERQT, Universitat de Barcelona, 08028 Barcelona, Spain.*

[d] *Dipartimento di Chimica e Centro di Strutturistica Diffrattometrica, Universitá di Ferrara, Italy*

Materials and Physical Measurements. The chemicals used were obtained from the following sources: Triethylenetetramine from S.D. Fine Chem (India). 2-hydroxy benzaldehyde from SRL (India). Cupric perchlorate hexahydrate was prepared by treating copper(II) carbonate with 1:1 $HClO_4$ and crystallized after concentration on water bath. All other chemicals and solvents were reagent grade materials and were used as received without further purification. The elemental analyses (C, H, N) were performed with a Perkin-Elmer model 240 C elemental analyzer. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer. The solution electrical conductivity and electronic spectra were obtained using a Unitech type U131C digital conductivity meter with a solute concentration of about 10^{-3} *M* and a Shimadzu UV 3100 UV-vis-NIR spectrophotometer respectively.The room temperature magnetic susceptibilities in the solid state were measured using a home built Gouy balance fitted with a polytronic d.c. power supply. The experimental magnetic susceptibilities were corrected for the diamagnetic response using Pascal's constants. Magnetic measurements were carried out on polycrystalline samples (ca. 30 mg) using a Quantum Design MPMS -7 SQUID magnetometer operating at a constant magnetic field of 5000 G between 1.8 and 300 K. The experimental magnetic moment was corrected for the diamagnetic contribution from the sample holder and the diamagnetic response from the sample, which was evaluated from Pascal's constants.

Crystallographic data of 1. $C_{54}H_{62}N_8O_{18}Cl_2Cu_4$, M_r = 1436.18, tetragonal, space group $P4_12_12$, a = 18.8646(2)Å, b = 18.8646(2)Å, c = 33.0288(3)Å, V = 11754.1(2)Å^3, ρ_{calcd} = 1.623 g /cm^3 and Z = 8. With the use of 14009 unique reflections collected at 293 K with Mo Kα radiation (λ = 0.71073 Å) out to θ range = 3.27 to 28.00 ° on a Nonius Kappa CCD single-crystal X-ray diffractometer, the structure was solved by using the SHELX-97 programme system and refined by full-matrix least squares methods. The refinement converged to final $R1$ = 0.0454, $wR2$ = 0.1192; and GOF = 1.072 with the largest difference peak and hole as 0.58 and –0.62 e Å^{-3} respectively. CCDC **619548.** See http://rsc.org for crystallographic data in cif or other electronic format.

Experimental procedure for synthesis of complex $[Cu_4(\mu_4\text{-}ClO_4)L_2]ClO_4{\cdot}4H_2O$ (1):
To the acetonitrile (15 ml) solution of $Cu(ClO_4)_2.6H_2O$ (0.371 g, 2.18 mmol), H_3L (0.5g, 1.09mmol) in MeOH (5ml) was added and stirred for 15 minutes followed by Et_3N (0.5 mL, 3.58 mmol) in acetonitrile was added dropwise. The mixture was stirred for 1.0 h, and the complex was precipitated as a green solid (~80 % yield).The solid was isolated, washed with cold methanol, and dried under vacuum over P_4O_{10}. The single crystals suitable for X-ray analysis was obtained from the above mixture during 7 days. Anal. Calcd for $C_{54}H_{62}N_8O_{18}Cl_2Cu_4$: Mwt = 1436.18. C, 45.16; H, 4.35; N, 7.80. Found: C, 44.94; H, 4.48; N, 7.72 . Molar conductance, Λ_M : (MeCN solution) 136 ohm^{-1} cm^2 mol^{-1}. UV-visible spectrum (CH_3CN):λ_{max} (ε_{max}) 613 (1100), 376 (20170), 306 (22840). Selected IR bands (KBr, cm^{-1}) 3400 vs , 1635 vs, 1600 s, 1537 m, 1469m, 1450 s, 1398w, 1344w, 1312m, 1241m, 1197w, 1153m, 1121s, 1109s, 1091vs, 917w, 768s, 626s.

Caution: Perchlorate-containing salts are potentially explosive!!! and should be handled in very small quantities.

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Table S1. Selected bond lengths (Å) and bond angles (^{0}) for 1.

Cu1-O1A	1.903(3)	Cu1-N1A	1.954(3)	Cu1-O2A	2.007(3)
Cu1-N2A	2.105(3)	Cu1-O1	2.220(3)	Cu2-O3A	1.896(3)
Cu2-N4A	1.957(3)	Cu2-O2A	1.985(3)	Cu2-N3A	2.051(3)
Cu2-O1	2.411(3)	Cu3-O1B	1.903(3)	Cu3-N1B	1.946(3)
Cu3-O2B	1.994(2)	Cu3-N2B	2.088(3)	Cu3-O2	2.307(3)
Cu4-O3B	1.890(3)	Cu4-N4B	1.955(3)	Cu4-O2B	2.021(3)
Cu4-N3B	2.077(3)	Cu4-O2	2.252(3)	Cl1-O1	1.484(3)
Cl1-O2	1.491(3)	Cl1-O3	1.558(4)	Cl1-O4	1.583(4)

O1A-Cu1-N1A	93.02(14)	O1A-Cu1-O2A	89.76(12)
N1A-Cu1-O2A	152.72(13)	O1A-Cu1-N2A	173.41(14)
N1A-Cu1-N2A	83.56(14)	O2A-Cu1-N2A	90.75(12)
O1A-Cu1-O1	96.57(13)	N1A-Cu1-O1	124.01(13)
O2A-Cu1-O1	82.49(10)	N2A-Cu1-O1	90.01(12)
O3A-Cu2-N4A	92.38(14)	O3A-Cu2-O2A	93.05(11)
N4A-Cu2-O2A	155.73(13)	O3A-Cu2-N3A	175.45(13)
N4A-Cu2-N3A	83.34(14)	O2A-Cu2-N3A	91.48(12)
O3A-Cu2-O1	90.04(13)	N4A-Cu2-O1	125.47(12)
O2A-Cu2-O1	78.18(10)	N3A-Cu2-O1	91.20(12)
O1B-Cu3-N1B	92.88(14)	O1B-Cu3-O2B	93.43(12)
N1B-Cu3-O2B	152.30(13)	O1B-Cu3-N2B	176.18(12)
N1B-Cu3-N2B	83.34(14)	O2B-Cu3-N2B	90.19(11)
O1B-Cu3-O2	91.65(13)	N1B-Cu3-O2	127.03(13)
O2B-Cu3-O2	79.70(10)	N2B-Cu3-O2	90.20(11)
O3B-Cu4-N4B	92.41(13)	O3B-Cu4-O2B	89.60(12)
N4B-Cu4-O2B	153.90(12)	O3B-Cu4-N3B	174.10(14)
N4B-Cu4-N3B	83.48(13)	O2B-Cu4-N3B	92.24(11)
O3B-Cu4-O2	95.91(13)	N4B-Cu4-O2	125.10(12)
O2B-Cu4-O2	80.47(10)	N3B-Cu4-O2	89.92(12)
O1-Cl1-O2	116.43(16)	O1-Cl1-O3	106.3(2)
O2-Cl1-O3	110.9(2)	O1-Cl1-O4	110.4(2)
O2-Cl1-O4	106.5(2)	O3-Cl1-O4	105.9(3)

Table S2. Configuration of the seven different spin states chosen to calculate the 6 *J* values. The energies of the spin states are referred to the energy of the high-spin (S=2) state.

Spin configurations				Energy (cm^{-1})
Cu_1	Cu_2	Cu_3	Cu_4	
↑	↑	↑	↑	0.00
↑	↓	↑	↑	ΔE_1= 35.88
↑	↑	↓	↑	ΔE_2= 36.58
↓	↑	↑	↑	ΔE_3= 35.88
↓	↓	↑	↑	ΔE_4= 0.15
↑	↓	↑	↓	ΔE_5= 72.36
↓	↑	↑	↓	ΔE_6= 72.49

Table S3. System of equations from the six energy differences of Table S2 (the $H = -2JS_1S_2$ Hamiltonian is employed).

$\Delta E_1 = 2J_1 + 2J_4 + 2J_6$
$\Delta E_2 = 2J_2 + 2J_3 + 2J_6$
$\Delta E_3 = 2J_1 + 2J_3 + 2J_5$
$\Delta E_4 = 2J_3 + 2J_4 + 2J_5 + 2J_6$
$\Delta E_5 = 2J_1 + 2J_2 + 2J_5 + 2J_6$
$\Delta E_6 = 2J_1 + 2J_2 + 2J_3 + 2J_4$

Table S4. *J* values as calculated for the molecule of **1** through DFT calculations using the above energy differences and equations.

J_1= 17.9 cm^{-1}
J_2= 18.2 cm^{-1}
J_3= 0.03 cm^{-1}
J_4= 0.04 cm^{-1}
J_5= 0.01 cm^{-1}
J_6= −0.01 cm^{-1}

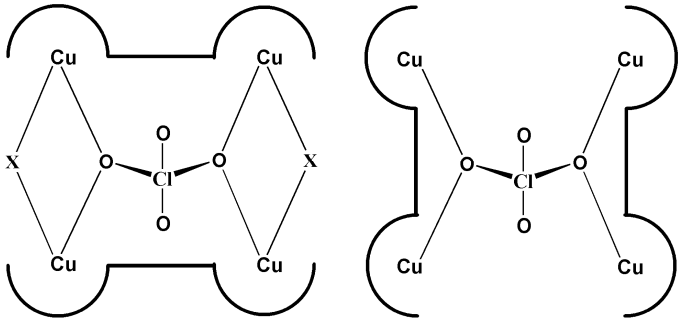

Fig. S1 Two different bridging arrangements directed by perchlorate anion. **Left**: Binucleating ligand scaffold an intradimer Cu-O-Cl-O-Cu separation. **Right**: Binucleating ligand scaffold an intradimer Cu-O-Cu separation.

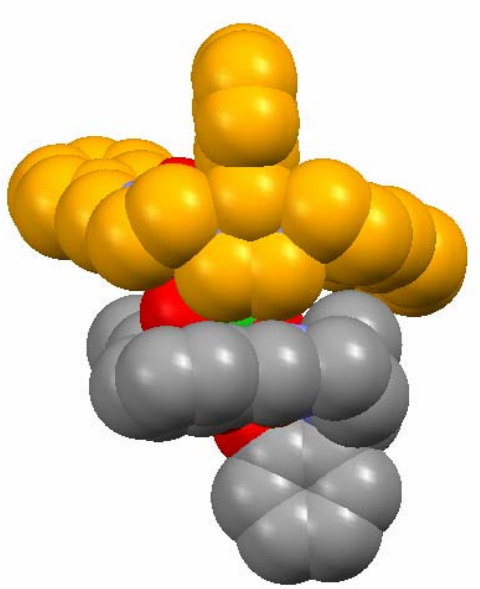

Fig. S2 Space filling model of two dimeric units mutually twisted and sandwiching the perchlorate anion. (Ligand carbon atoms are shown in yellow and grey colours; red, oxygen; green, chlorine.)

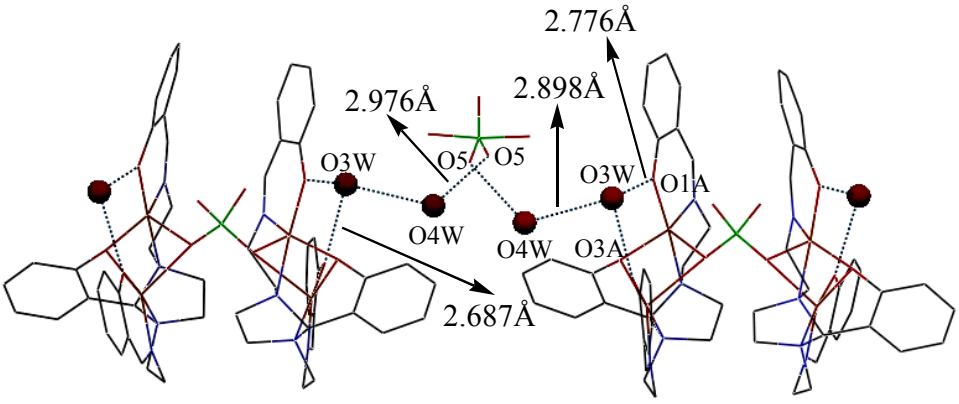

Fig. S3 Two tetrameric unit held together by anion-water intermolecular hydrogen bonding.

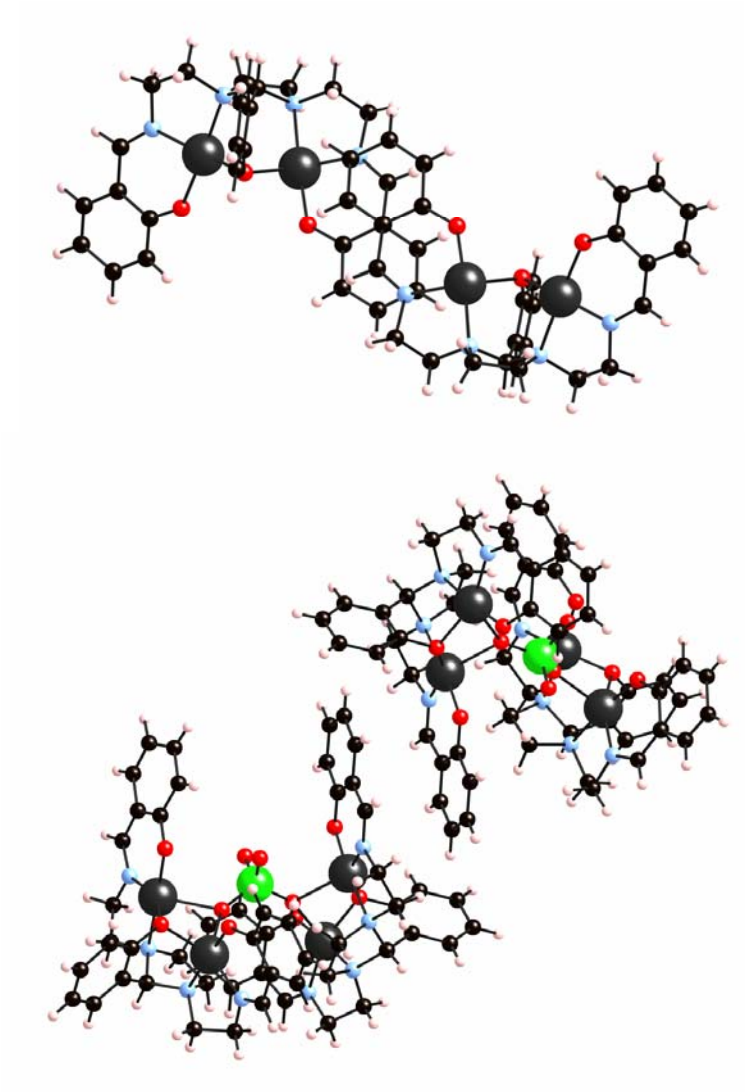

Fig. S4 Two views of the intermolecular interaction within the crystal lattice of **1** through a pseudo π–π stacking system. Top; view of only two Cu(II) pairs from different tetranuclear clusters, where the stacking is viewed perpendicular to the π–rings. Bottom; two interacting tetranuclear units of **1**, showing a side view of the π–π interaction in the distance of 4.231Å.

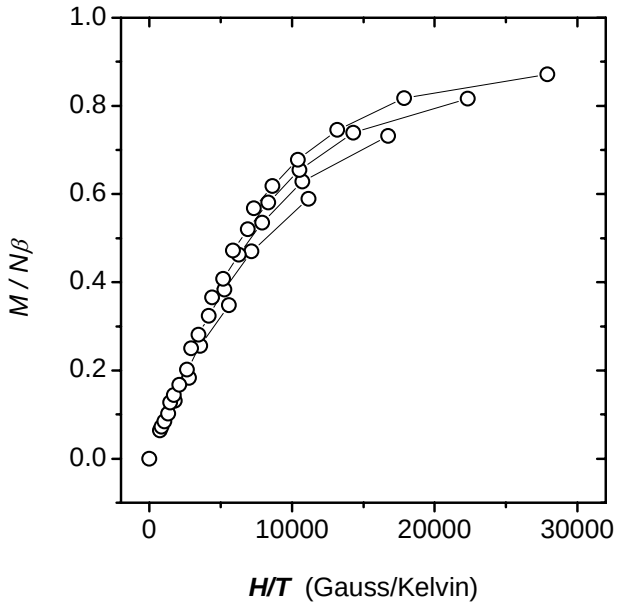

Fig. S5 Variable temperature isofield reduced magnetization *versus H/T* curves for complex **1**, performed at 0.5, 1, 2, 3, and 5 Tesla.