Supporting Infromation for

A Magnetically highly frustrated Cu^{II}_{27} Coordination Cluster Containing a Cu_{18} Folded-Sheet Motif

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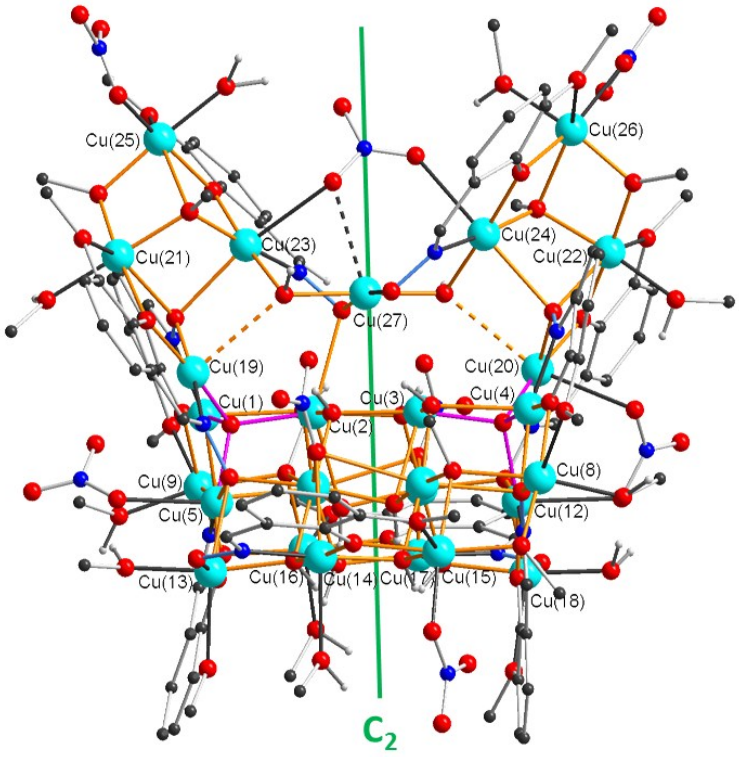

Fig. S1: Illustiration of the pseudo-C_2 symmetry in **1**.

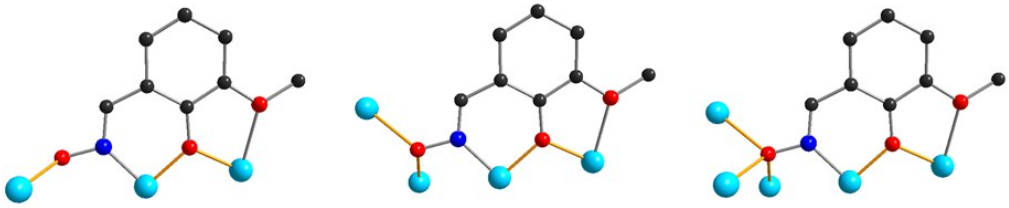

Fig. S2: Coordination modes of the $(vanox)^{2-}$ ligands in **1**.

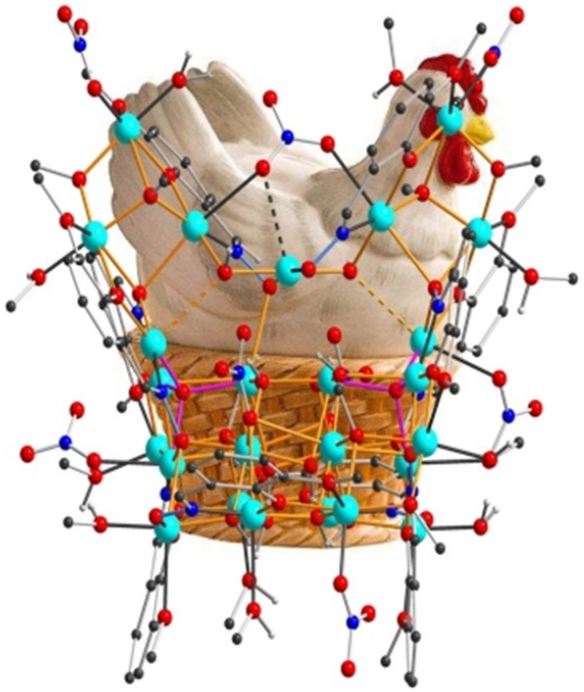

Fig. S3: "Chicken in a basket" motif of **1**.

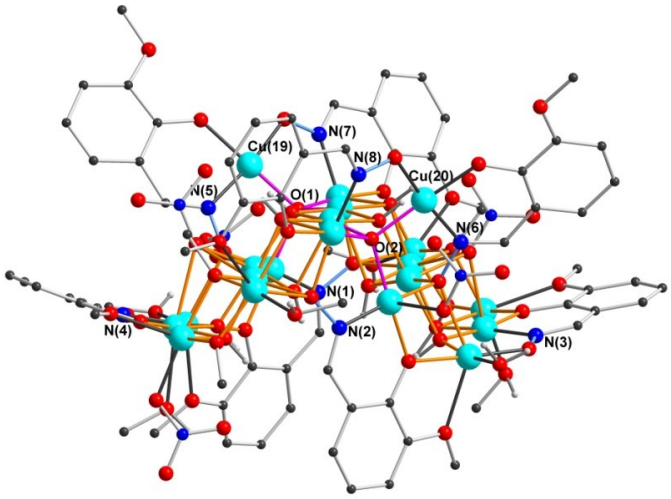

Fig. S4: Different view of the folded sheet part of Cu(1) to Cu(18) of **1** with a dihedral angle of 101.7° between the mean planes of each of the two halves of the sheet.

S5. Crystallography, Tables of crystal data, selected bond lengths and angles for **1**.

The crystallographic measurement was carried out on using Bruker Smart APEX diffractometer with Si-monochromated radiation of wavelength 0.8000 Å on the SCD beamline of the ANKA Synchroton Source, Karlsruhe. The structure was solved by direct methods using SHELXS and refined with full-matrix least squares on F^2 using SHELXL-97 and SHELXL-2014.[1] Some lattice MeOH (18 in the unit cell, 4½ per cluster) were badly disordered, and their contribution to the structure factors was calculated using the SQUEEZE option in PLATON.[2] In the refinement, the calculated structure factors included contributions from this .fab file. The atoms of these disordered ("SQUEEZEd") molecules are included in the chemical formula.

All ordered non-H atoms in the cluster were refined anisotropically. Disordered atoms were refined using isotropic partially occupancy atoms, with geometrical similarity restraints as appropriate. A disordered vanox ligand was refined using two rigid hexagons for the aromatic rings. Organic hydrogen atoms were placed in calculated positions. O-H H-atoms were mostly refined with isotropic U set to 1.2 U(eq) for the O to which they were bonded, and with O-H distances restrained to 0.92(4) Ang. Not every O-bonded H-atom could be located, however, and no attempt was made to model the H-atoms of the lattice MeOH molecules.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC ..... Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK:

http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, e-mail: data_request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

All graphics were generated using Diamond.[3]

Empirical formula	$C_{105}H_{184}Cu_{27}N_{20}O_{104}$	F(000)	10276
Formula weight [g/mol]	5106.29	Calculated density [g/cm^3]	1.932
Crystal System	monoclinic	Absorption coefficient [mm^{-1}]	4.581
Space group	$P2_1/c$	Temperature [K]	150
a [Å]	31.939(3)	Reflections collected	194764
b [Å]	18.8704(16)	Unique data	39592
c [Å]	32.730(3)	R_{int}	0.0595
α [°]	90	Data with I > 2σ(I)	32186
β [°]	117.116(2)	Parameters/restraints	2235 / 24
γ [°]	90	wR_2	0.1490
Volume	17558(3)	R_1 [I > 2σ(I)]	0.0507
Z	4	GooF	1.046
Crystal size [mm]	0.18 × 0.15 × 0.12	Largest diff. peak / hole [e Å^{-3}]	+1.86 / -1.08

S6. Chemicals and Instrumentation.

Commercially available reagents were used without further purification unless otherwise stated.

o-Vanillinoxime (vanox) was prepared according to the procedures described in the literature.[4]
A suspension of 3.31g (24.2 mmol) of *o*-vanillin in 11ml H_2O was stirred while heating to 45°C. A solution containing 1.80g (26.1 mmol) $NH_2OH{\cdot}HCl$ and 1.78g (21.8 mmol) CH_3CO_2Na was added and the reaction was heated with stirring at 80°C for 2h. Upon cooling to room temperature the resulting white microcrystalline precipitate was filtered and washed with cold H2O and recrystallized from EtOH. The resulting compound is light sensitive.

Elemental analysis (C, H and N) was performed by Vario EL (Elementar Analysen System GmbH) from Perkin Elmer. Fourier transform infrared spectra (FT-IR) were recorded as KBr pellets on a Perkin Elmer Spectrum GX in the range of 4000 to 400 cm^{-1}.
Magnetic susceptibility measurements were obtained with a Quantum Design SQUID magnetometer MPMS-XL. The measurements were performed on 14.5 mg of a polycrystalline powder.

S7. Synthesis and characterization of **1**.

0.042 g (0.25 mmol) H_2vanox, 0.040 g (1.0 mmol) NaOH were solved in 10.0 ml MeOH and put to a solution of 0.302 g (1.25 mmol) $Cu(NO_3)_2{\cdot}3H_2O$ in 15.0 ml MeOH. The dark green solution is stirred for 10 minutes at room temperature, and without any filtering left to stand for crytalization. After 2 weeks complex **1** crystallizes as dark black cubes.
Yield: 0.044 g (20.5% related to Cu)
Elemental analysis for $C_{105}H_{184}Cu_{27}N_{20}O_{74}$ (%): calculated: C: 27.259, H: 4.008, N: 6.055;
found: C: 27.13, H: 3.82, N: 6.22
IR (KBr): $\tilde{\nu}$ = 3430 m, 2427 w, 1602 m, 1560 w, 1466 m, 1439 w, 1384 s, 1281 m, 1247 m, 1221 m, 1106 m, 1046 m, 974 m, 839 w, 867 w, 770 w, 736 w, 648 w, 571 w, 467 w cm^{-1}.

1. G. M. Sheldrick, *Acta Cryst.*, 2008, A64, 112-122.
2. A.L. Spek, A.L., *J. Appl. Cryst.*, 2003, **36**, 7-13
3. K. Brandenburg, *Diamond 3.1, Cryst. IMPACT GbR*, 2008, Bonn**,** Deutschland.
4. I. J. Hewitt, Y. Lan, C. E. Anson, J. Luzon, R. Sessoli, and A. K. Powell, *Chem. Commun.*, 2009, **3**, 6765–7.