Electronic Supplementary Information (ESI)

A Hexaicosametallic Copper(II) Phosphonate

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Instrumentation:

Melting points were measured using a JSGW melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT IR spectrophotometer operating at 400−4000 cm−1. Elemental analyses of the compounds were obtained from Thermoquest CE instruments CHNS-O, EA/110 model. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Micromass Quattro II triple quadrupole mass spectrometer.

Magnetic Measurements:

Variable-temperature (2.0 – 300 K) direct current (dc) magnetic susceptibility under an applied field of 1000 G where carried out with a Quantum Design SQUID magnetometer. The magnetic susceptibility data were corrected for the diamagnetism of the constituent atoms and the sample holder.

X-ray Crystallography:

Data were collected on Bruker APEX IICCD diffractometer (MoK_{α}, λ = 0.71073 Å). Complete hemispheres of data were collected using ω-scans (0.3°, up to 30 s/frame). Integrated intensities were obtained with SAINT+,[1]and when they were corrected for absorption SADABS was used.[2]Structure solution and refinement was performed with the SHELXTL-package.[3] The structures were solved by direct methods and completed by iterative cycles of DF syntheses and full-matrix least-squares refinement against F^2.[4] All the other non-hydrogen atoms were refined with anisotropic displacement parameters. All the hydrogen atoms on the carbon frameworks were included in the final stages of the refinement and were refined with a typical riding model. Some solvent molecules could not be modeled satisfactorily as they were located on the symmetry elements of the space group. Therefore the Olex/Mask[5] was used to remove such disordered units from the respective overall intensity data. The details of the masked electron density areappended to the respective cif files. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge CrystallographicData Centre, 12, Union Road, Cambridge CB2 1EZ, U.K. Fax: +44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk].

References:

1 *SMART & SAINT Software Reference Manuals, version 6.45; Bruker Analytical X-ray Systems*, Inc.: Madison, WI, 2003.

2 G. M. Sheldrick, *SADABS a Software for Empirical AbsorptionCorrection, version 2.05*; University of Göttingen: Göttingen, Germany, 2002**.**

3 G. M. Sheldrick, *SHELXTL, version 6.12; Bruker AXS Inc.*Madison, WI, 2001.

4 G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*, University of Göttingen: Göttingen, Germany, 1997.

5 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *OLEX2*: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.*, 2009, **42**, 339.

Mask Details

Electron count 1129.9 (void of 11120 Å) per unit cell accounts for 6 CH_3CN and 15 water molecules (1128 total no. of calculated e^- (Z=4))

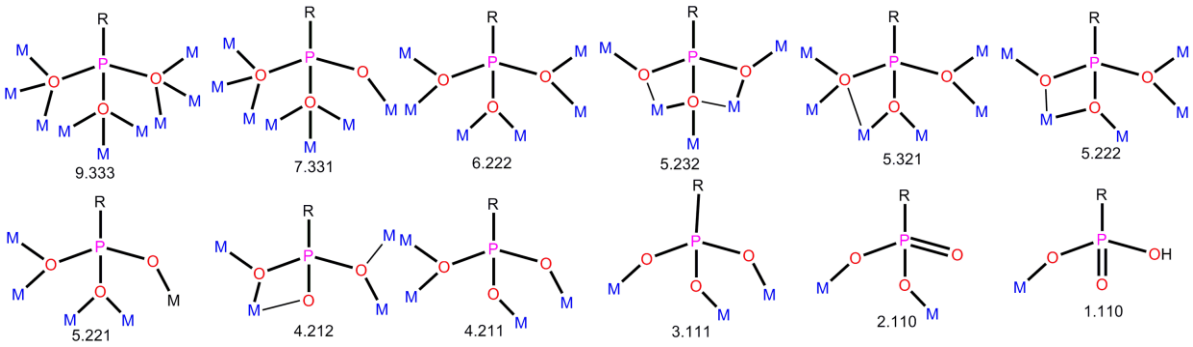


Chart S1. Possible coordination modes of phosphonate ligands using the Harris notation.[8]

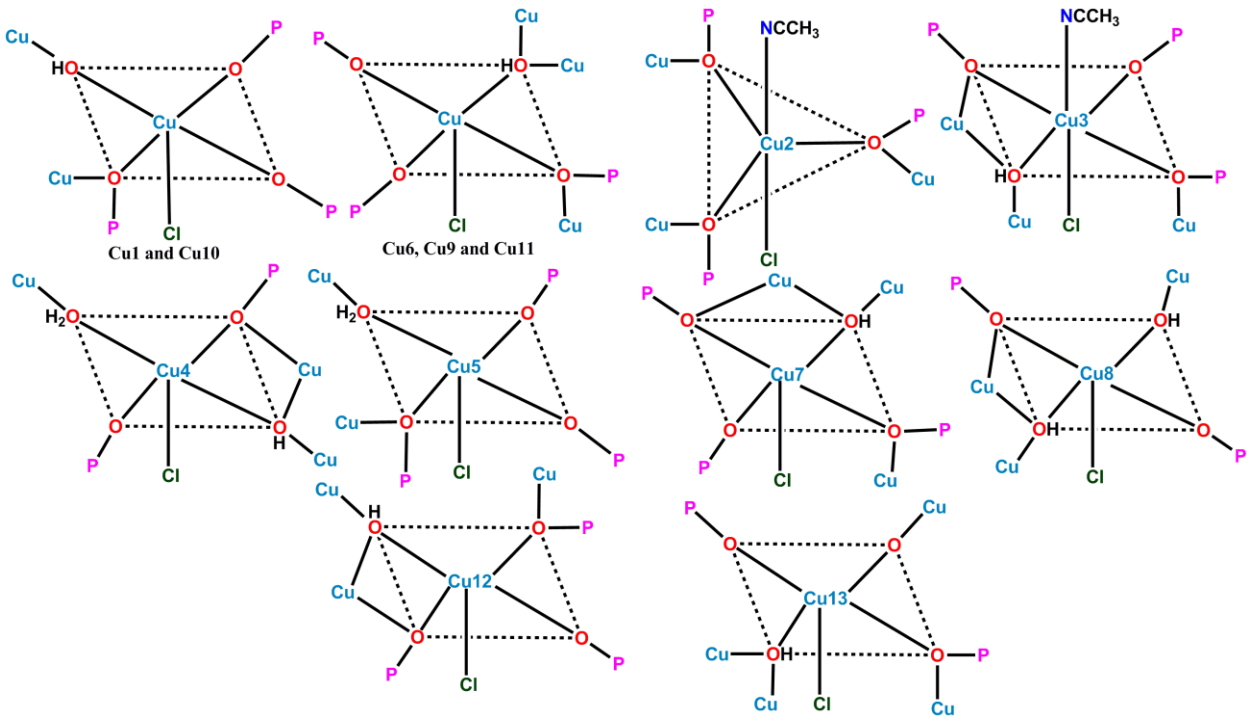


Chart S2 Ten different coordination environments present for the thirteen copper centers present in the asymmetric unit of **1** (for the numbering scheme see Fig. 2a)

References:

6 (a) S. G. Harris, *Ph.D. Thesis*, The University of Edinburgh, 1999; (b) R. A. Coxall, S. G. Harris, D. K. Henderson, S. Parsons, P. A. Taskerand R. E. P. Winpenny, *J. Chem. Soc. Dalton Trans.*, 2000, 2349.

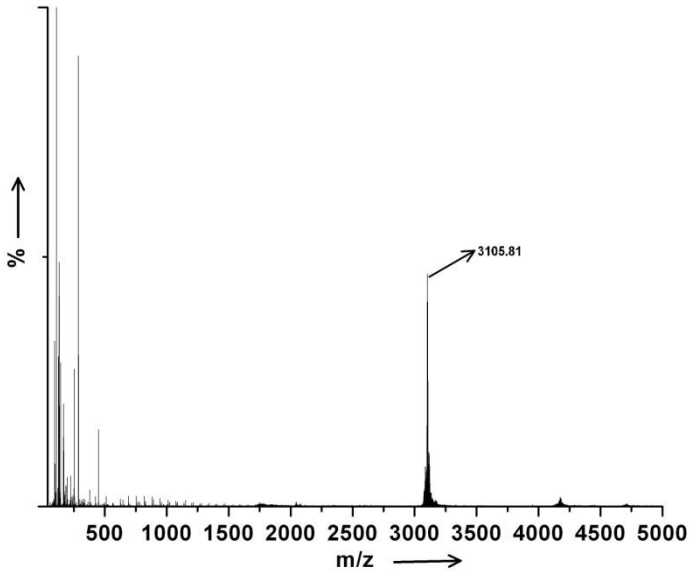
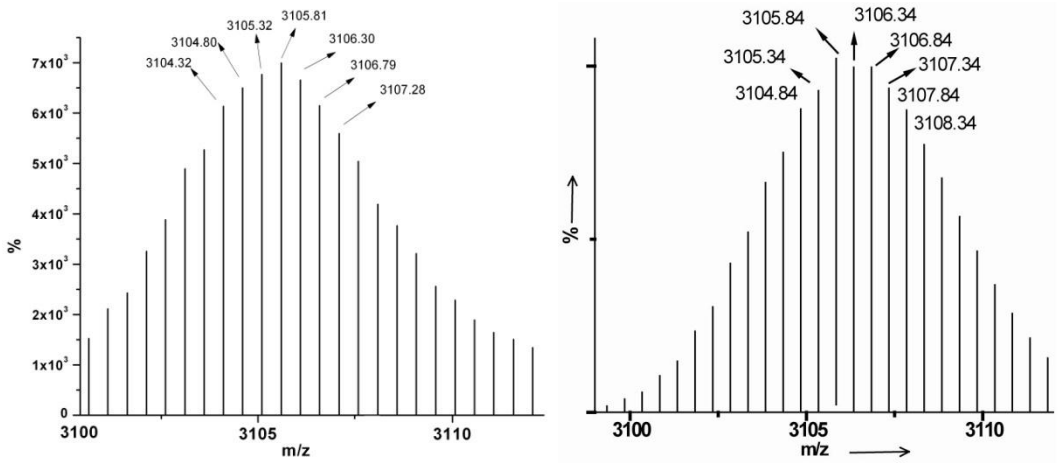


Fig.S1. (a) The full rang**e** ESI-MS spectrum of **1** recorded under negative ion ionization conditions.



(b) (c)

Fig. S1 (b) Experimental mass spectral pattern for the parent ion peak (c) Simulated mass spectral pattern for the parent ion peak showing a close resemblance with the experimental spectrum.

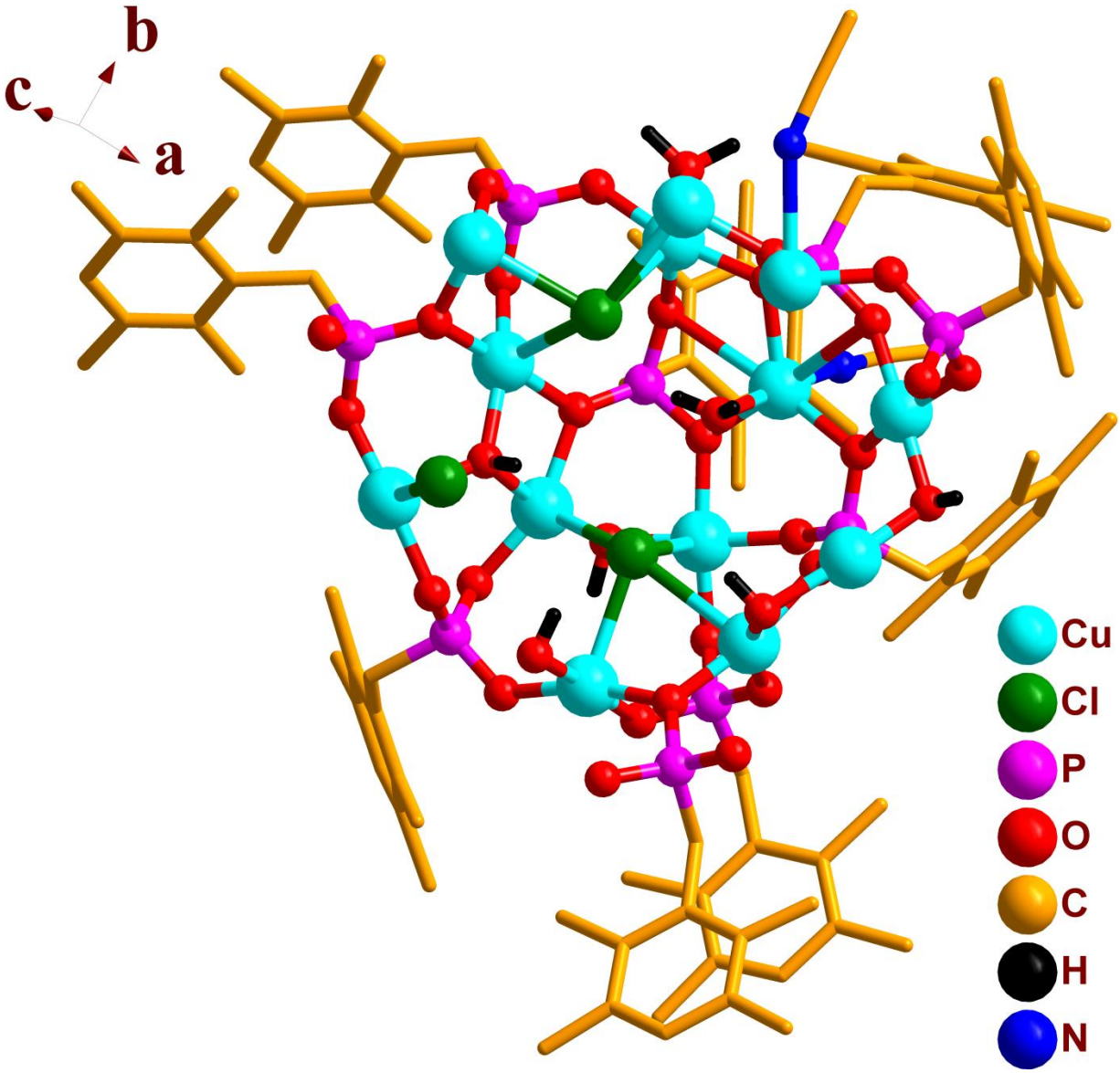


Fig. S2 Asymmetric unit contents of **1**.Some hydrogen atoms of the phosphonate and solvent molecules have been removed for clarity.

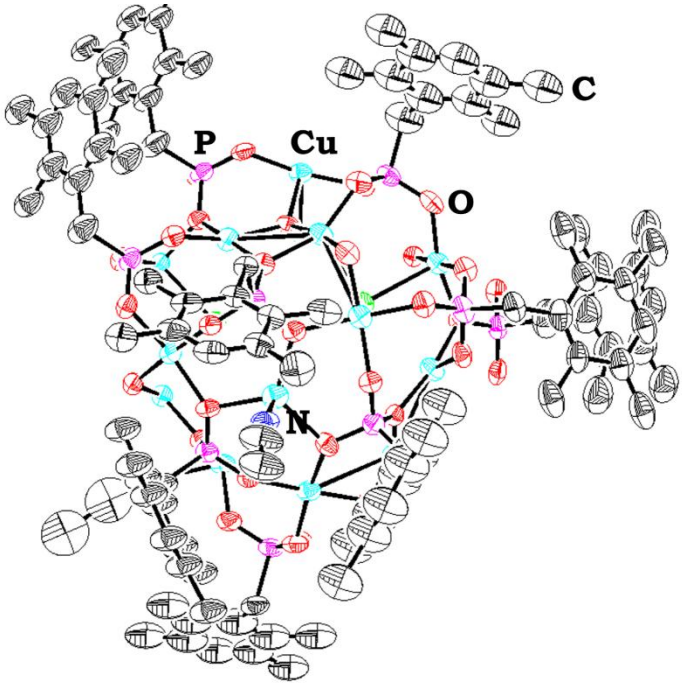


Fig. S3 ORTEP diagram of **1** with 50 % thermal ellipsoids (asymmetric unit). Hydrogen atoms, carbon of the phosphonate and solvent molecules have been removed for clarity.

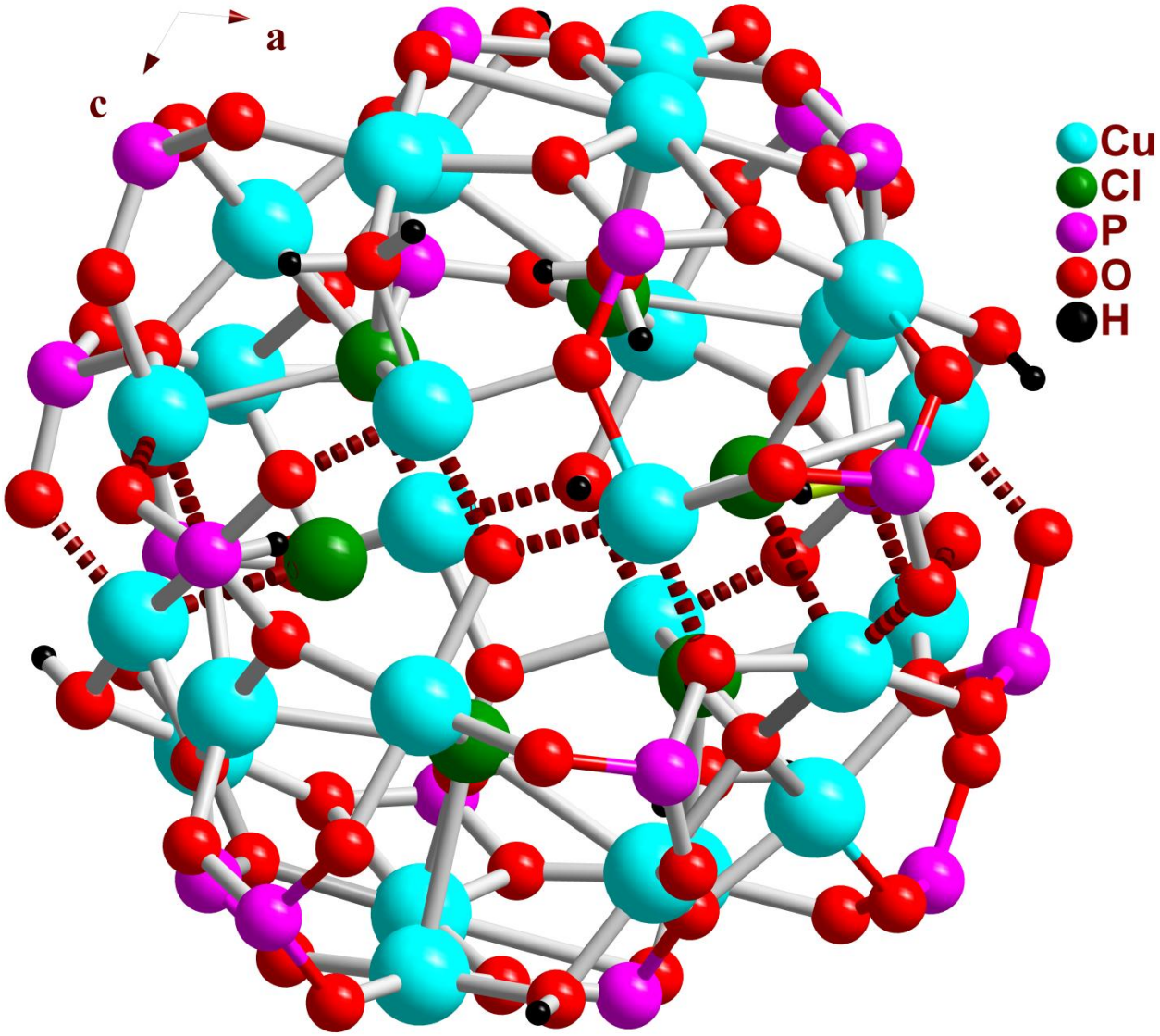
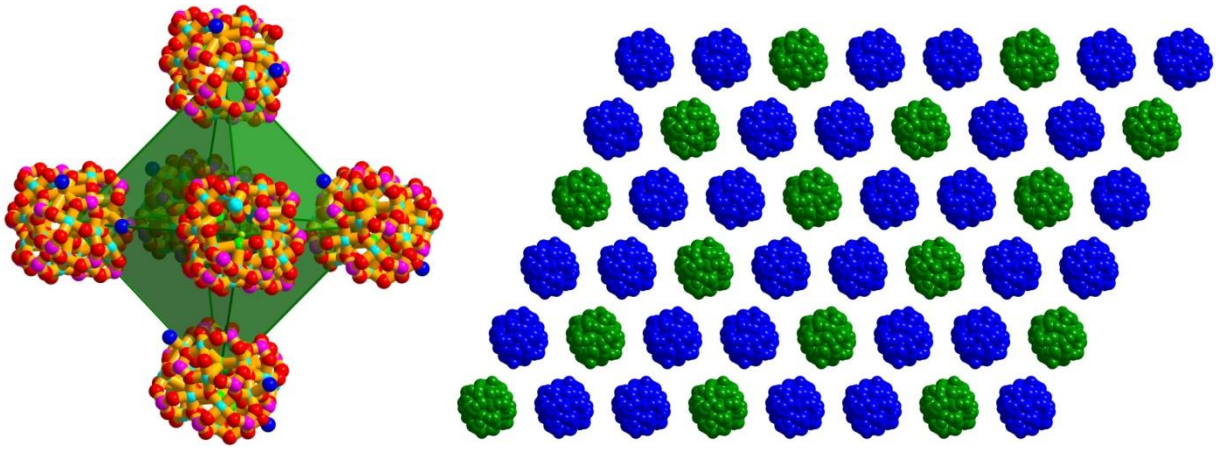


Fig. S4 Connection of the two hemispheres of **1.**



(a) (b)

Fig. S5 (a) Octahedral packing arrangement of the molecules of **1**in its crystal lattice (b) Packing diagram of **1**. View along 'b' axis. Each molecule of **1** is surrounded by six other similar Cu_{26} cages.

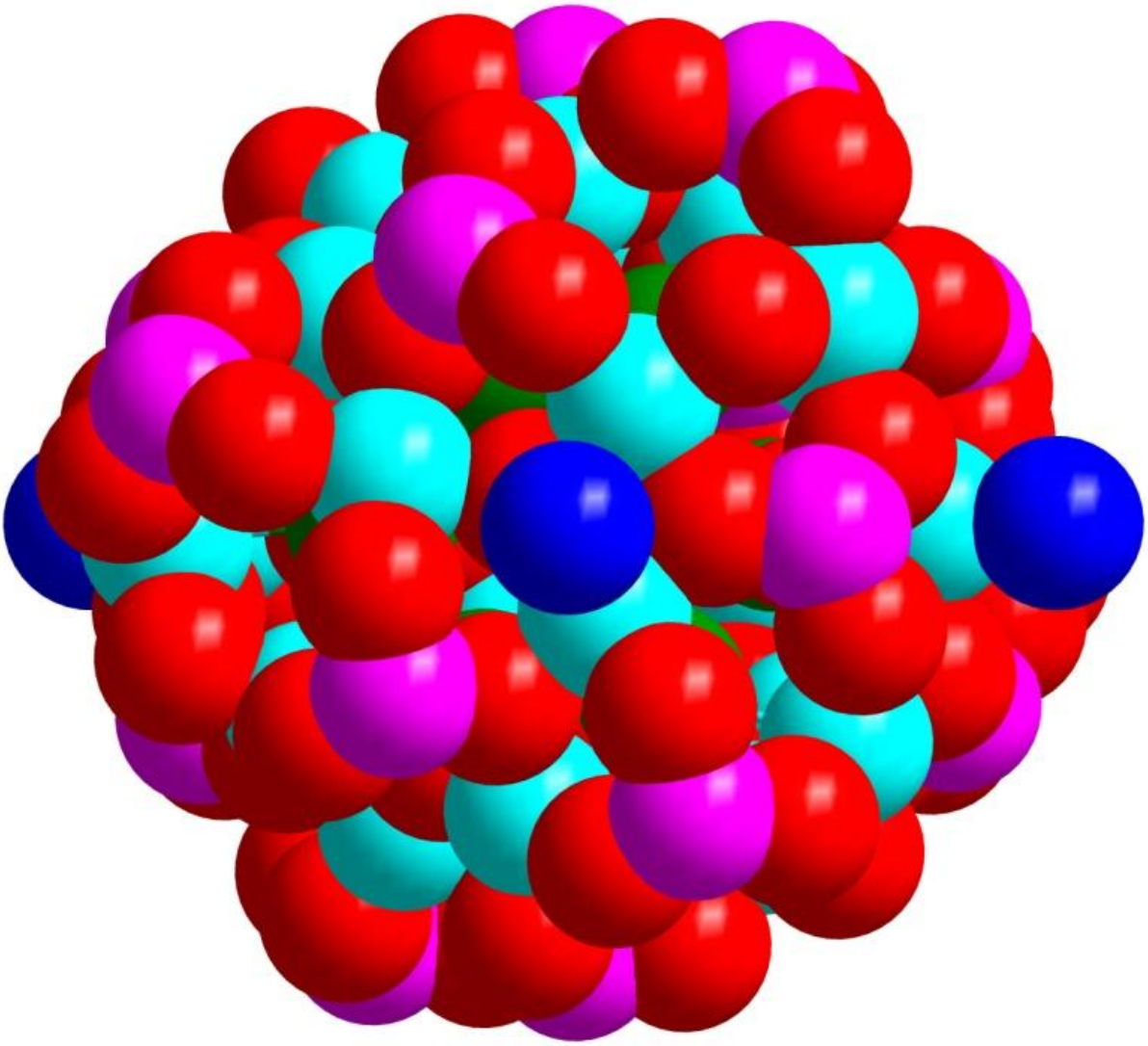


Fig. S6 Space filling view of **1**.

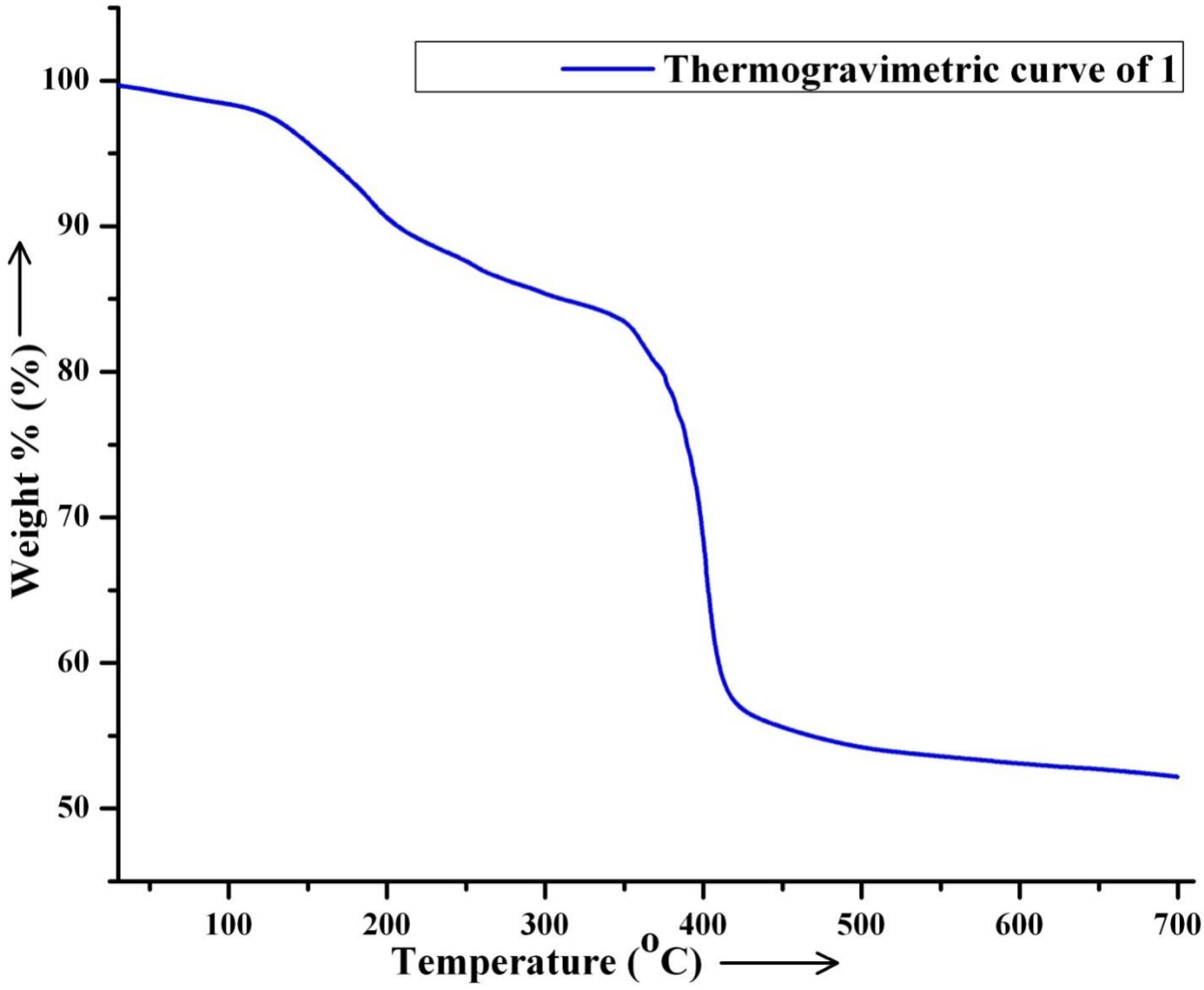


Fig. S7 TGA trace of **1**.

Before 98 °C it does not show significant weight loss. From 100 °C to 202 °C it loses 8-9 % of its weight which corresponds to loss 6 acetonitrile and 15 water molecules. From 202 °C to 470 °C it shows a weight loss around 40 % which may corresponds to loss of 2,3,5,6-$(Me)_4C_6H$-CH_2- part of the phosphonic acid.

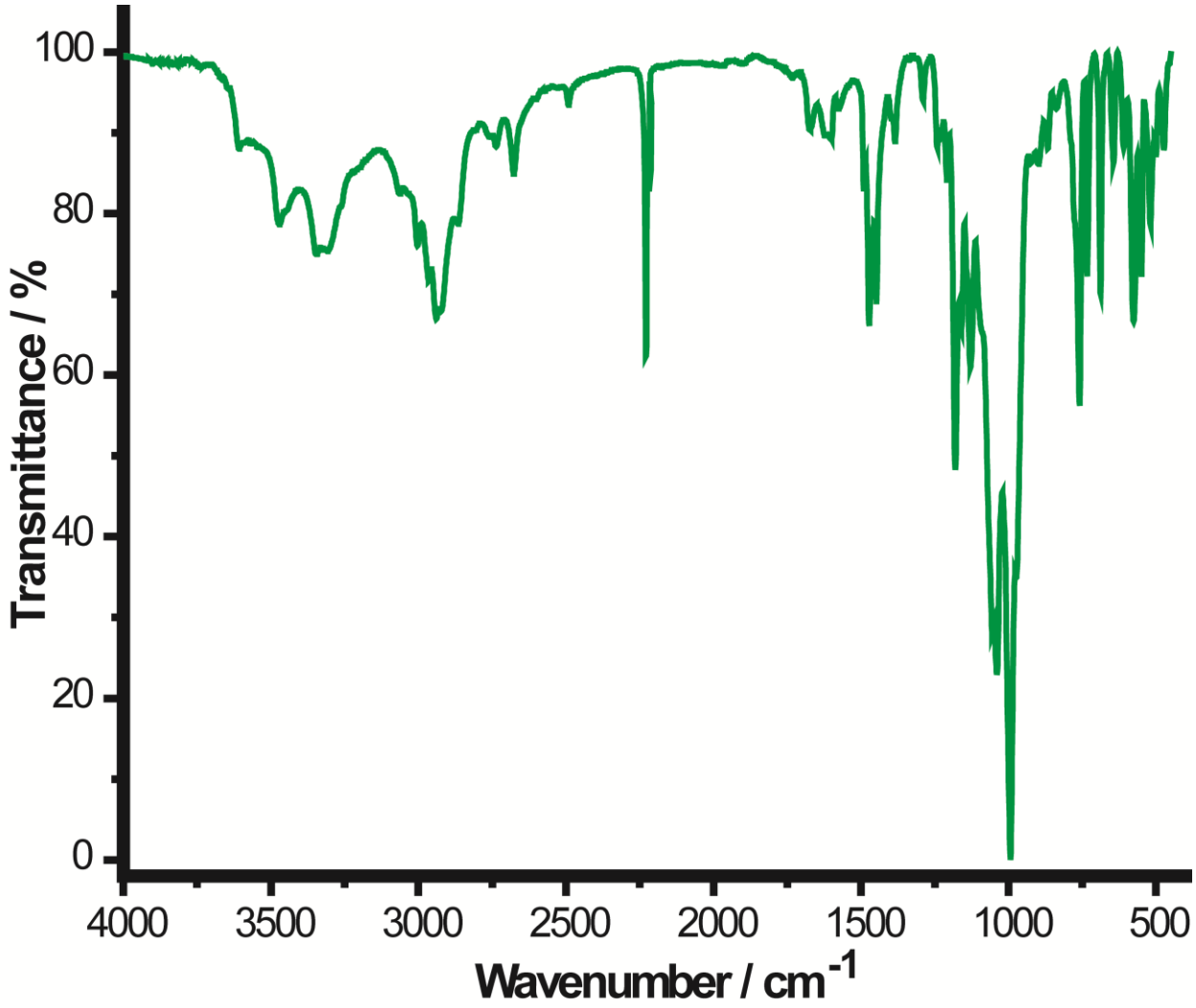
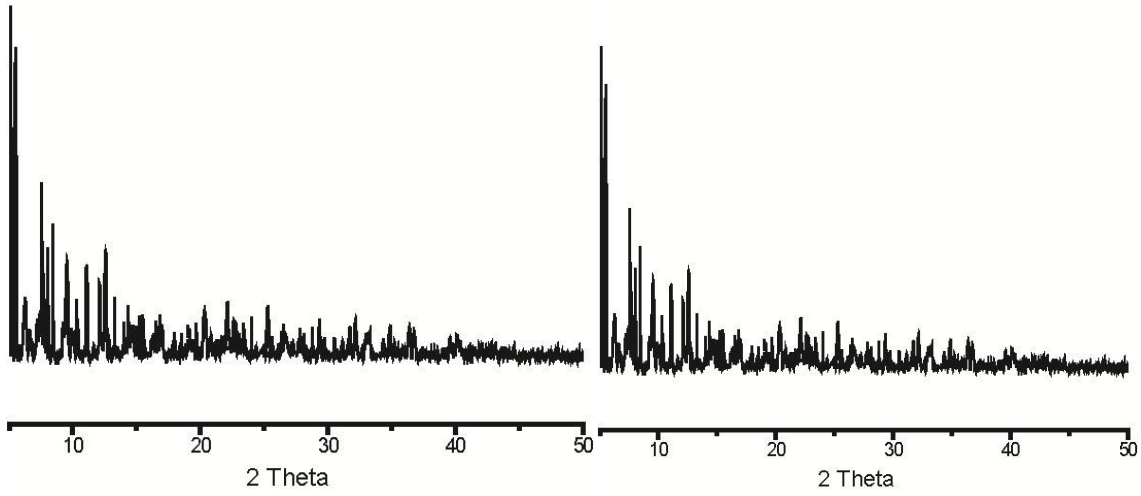


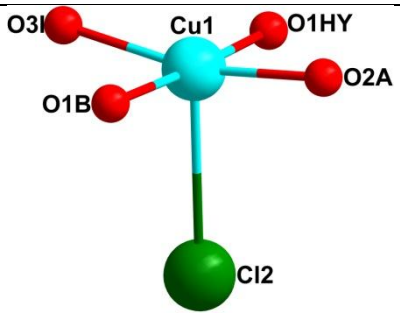
Fig. S8 IR spectrum of **1.**

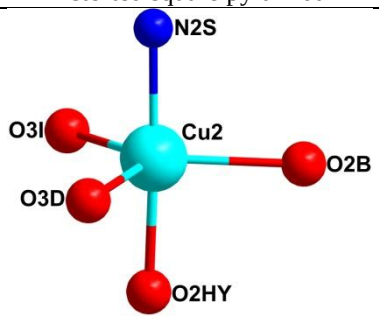
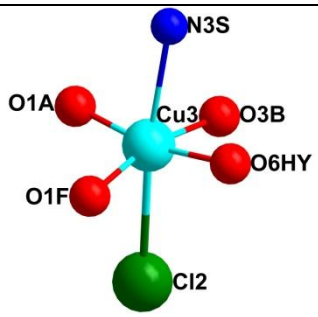
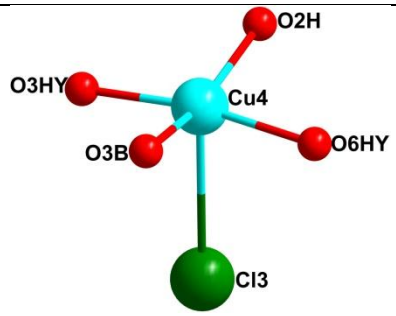
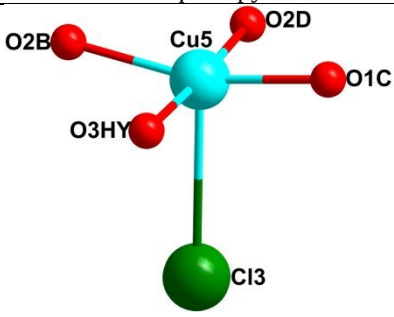


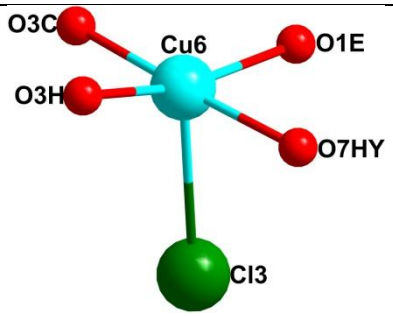
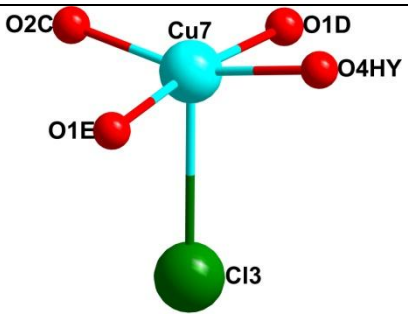
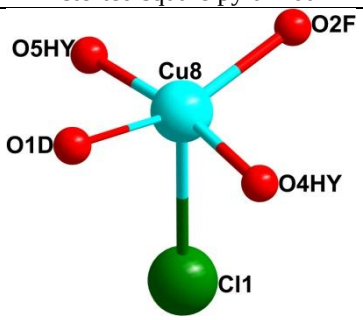
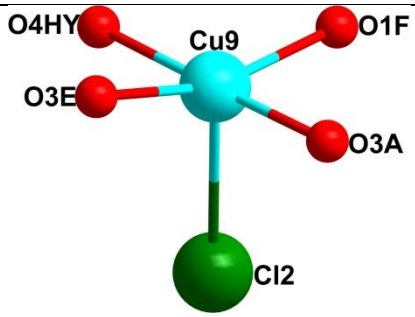
(a) (b)

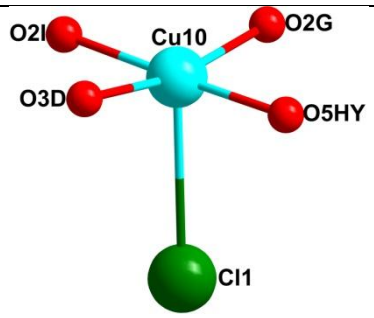
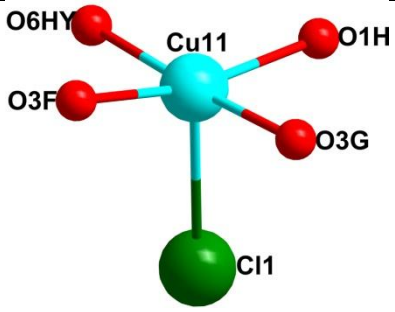
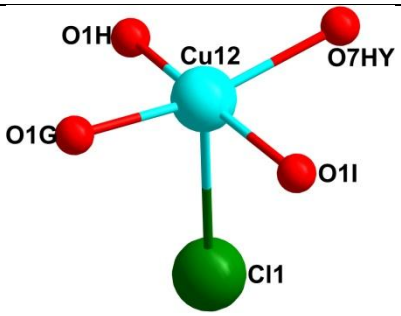
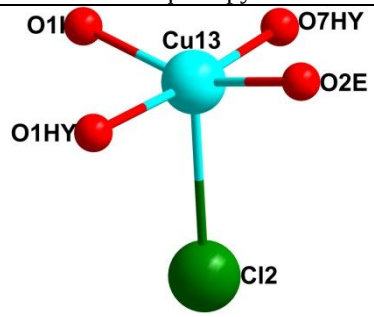
Fig. S9 (a) PXRD from single crystal diffraction data (b) PXRD of the bulk sample

Table S1. Coordination geometries, bond distances (Å) and bond angles (°) of **1.**

Coordination environment around metal ion	**Bond distances (Å)**			**Bond angles (°)**			
	Cu1	Cl2	2.923(2)	O1HY	Cu1	O2A	87.8(2)
	Cu1	O2A	1.920(5)	O1B	Cu1	O3I	86.5(2)
	Cu1	O1B	1.915(5)	O1B	Cu1	O2A	95.1(2)
	Cu1	O3I	1.981(5)	O2A	Cu1	O3I	167.0(2)
	Cu1	O1HY	1.899(5)	O1HY	Cu1	O3I	90.5(2)
				O1HY	Cu1	O1B	177.0(2)

Distorted square pyramidal							
 Distortedtrigonalbipyramidal	Cu2	O2B	2.127(5)	O3D	Cu2	O3I	118.4(2)
	Cu2	O3D	2.108(5)	O3I	Cu2	O2B	120.7(2)
	Cu2	O3I	2.122(5)	O2HY	Cu2	O2B	88.26(19)
	Cu2	O2HY	1.959(5)	N2S	Cu2	O2HY	177.5(3)
	Cu2	N2S	1.887(7)	N2S	Cu2	O3I	90.8(3)
				N2S	Cu2	O3D	94.3(3)
				N2S	Cu2	O2B	93.5(3)
				O2HY	Cu2	O3I	86.8(2)
				O2HY	Cu2	O3D	86.3(2)
				O3D	Cu2	O2B	120.13(19)
 Distorted octahedral	Cu3	Cl2	3.013(2)	O1A	Cu3	O3B	96.2(2)
	Cu3	O1A	1.887(5)	O1A	Cu3	O1F	93.4(2)
	Cu3	O3B	1.954(5)	O1A	Cu3	N1	87.9(3)
	Cu3	O1F	1.957(5)	O6HY	Cu3	N1	78.8(3)
	Cu3	O6HY	1.994(5)	O1F	Cu3	N1	106.7(3)
				O1F	Cu3	O6HY	91.9(2)
				O3B	Cu3	N1	84.3(3)
				O3B	Cu3	O6HY	81.1(2)
				O3B	Cu3	O1F	165.7(2)
				O1A	Cu3	O6HY	166.6(2)
 Distorted square pyramidal	Cu4	Cl3	2.841(2)	O2H	Cu4	O3B	158.0(2)
	Cu4	O3B	1.974(5)	O2H	Cu4	O6HY	95.6(2)
	Cu4	O2H	1.916(5)	O3HY	Cu4	O3B	92.3(2)
	Cu4	O3HY	1.912(5)	O3HY	Cu4	O2H	93.5(2)
	Cu4	O6HY	2.004(5)	O3HY	Cu4	O6HY	170.5(2)
				O3B	Cu4	O6HY	80.3(2)
 Distorted square pyramidal	Cu5	Cl3	2.868(2)	O2D	Cu5	O2B	86.0(2)
	Cu5	O2B	1.993(5)	O1C	Cu5	O2B	164.5(2)
	Cu5	O1C	1.927(5)	O2D	Cu5	O1C	92.0(2)
	Cu5	O2D	1.910(5)	O3HY	Cu5	O2B	91.2(2)
	Cu5	O3HY	1.908(5)	O3HY	Cu5	O1C	90.3(2)
				O3HY	Cu5	O2D	176.9(2)
				O3HY	Cu5	Cl3	85.31(12)

 Distorted square pyramidal	Cu6	Cl3	2.683(2)	O3C	Cu6	O3H	90.4(2)
	Cu6	O3H	1.921(4)	O3C	Cu6	O7HY	177.9(2)
	Cu6	O3C	1.929(4)	O1E	Cu6	O7HY	87.1(2)
	Cu6	O1E	1.968(4)	O3H	Cu6	Cl3	109.78(17)
	Cu6	O7HY	2.016(3)	O3H	Cu6	O1E	164.6(2)
				O3H	Cu6	O7HY	90.8(2)
				O7HY	Cu6	Cl3	84.43(14)
				O3C	Cu6	Cl3	96.74(16)
				O1E	Cu6	Cl3	85.19(15)
				O3C	Cu6	O1E	91.3(2)
 Distorted square pyramidal	Cu7	Cl3	2.845(2)	O1D	Cu7	O1E	172.0(2)
	Cu7	O2C	1.907(5)	O2C	Cu7	O1D	95.3(2)
	Cu7	O1D	1.937(5)	O2C	Cu7	O4HY	160.7(2)
	Cu7	O1E	1.945(5)	O2C	Cu7	O1E	91.6(2)
	Cu7	O4HY	2.001(5)	O1D	Cu7	O4HY	81.0(2)
				O1E	Cu7	O4HY	93.9(2)
 Distorted square pyramidal	Cu8	Cl1	2.729(2)	O1D	Cu8	Cl1	99.50(15)
	Cu8	O1D	1.987(5)	O1D	Cu8	O4HY	80.1(2)
	Cu8	O2F	1.946(5)	O2F	Cu8	Cl1	107.55(16)
	Cu8	O4HY	1.989(5)	O2F	Cu8	O1D	152.5(2)
	Cu8	O5HY	1.890(5)	O2F	Cu8	O4HY	95.4(2)
				O4HY	Cu8	Cl1	89.14(15)
				O5HY	Cu8	Cl1	88.06(17)
				O5HY	Cu8	O4HY	170.2(2)
				O5HY	Cu8	O2F	94.3(2)
				O5HY	Cu8	O1D	91.2(2)
 Distorted square pyramidal	Cu9	Cl2	2.698(1)	O3E	Cu9	O4HY	89.5(2)
	Cu9	O3A	1.914(5)	O1F	Cu9	Cl2	86.03(15)
	Cu9	O3E	1.921(4)	O1F	Cu9	O4HY	88.0(2)
	Cu9	O1F	1.978(4)	O4HY	Cu9	Cl2	82.52(15)
	Cu9	O4HY	2.023(4)	O3A	Cu9	O1F	90.8(2)
				O3A	Cu9	O4HY	178.8(2)
				O3E	Cu9	Cl2	110.93(18)
				O3E	Cu9	O3A	91.5(2)
				O3E	Cu9	O1F	162.4(2)
				O3A	Cu9	Cl2	97.86(18)
				O4HY	Cu9	Cl2	82.73(11)

 Distorted square pyramidal	Cu10	O3D	1.980(5)	O2G	Cu10	O2I	92.2(2)
	Cu10	O2G	1.924(5)	O2I	Cu10	O3D	86.3(2)
	Cu10	O2I	1.933(5)	O5HY	Cu10	O3D	91.1(2)
	Cu10	O5HY	1.908(5)	O5HY	Cu10	O2G	89.8(2)
				O5HY	Cu10	O2I	176.5(2)
				O2G	Cu10	O3D	166.2(2)
 Distorted square pyramidal	Cu11	Cl1	2.644(2)	O3F	Cu11	Cl1	109.02(17)
	Cu11	O3F	1.897(6)	O3F	Cu11	O3G	88.4(2)
	Cu11	O3G	1.937(5)	O3F	Cu11	O1H	165.4(2)
	Cu11	O1H	1.949(5)	O3F	Cu11	O6HY	91.4(2)
	Cu11	O6HY	2.009(5)	O3G	Cu11	Cl1	97.38(16)
				O3G	Cu11	O1H	90.8(2)
				O3G	Cu11	O6HY	177.1(2)
				O1H	Cu11	O6HY	88.6(2)
				O6HY	Cu11	Cl1	85.40(15)
				O1H	Cu11	Cl1	85.56(15)
 Distorted square pyramidal	Cu12	Cl1	2.901(3)	O1H	Cu12	O1I	168.9(2)
	Cu12	O1G	1.890(5)	O1H	Cu12	O7HY	93.6(2)
	Cu12	O1H	1.937(5)	O1I	Cu12	O7HY	81.1(2)
	Cu12	O1I	1.943(5)	O1G	Cu12	O1H	92.0(2)
	Cu12	O7HY	2.003(5)	O1G	Cu12	O7HY	161.3(2)
				O1G	Cu12	O1I	96.0(2)
				O1G	Cu12	Cu13	128.21(17)
 Distorted square pyramidal	Cu13	Cl2	2.746(2)	O2E	Cu13	Cl2	104.27(18)
	Cu13	O2E	1.929(5)	O2E	Cu13	O1I	158.1(2)
	Cu13	O1I	1.970(5)	O7HY	Cu13	Cl2	89.55(15)
	Cu13	O1HY	1.895(5)	O7HY	Cu13	Cu12	42.42(14)
	Cu13	O7HY	1.990(5)	O1I	Cu13	Cl2	97.43(14)
				O1HY	Cu13	Cl2	88.54(18)
				O1HY	Cu13	O2E	92.1(2)

For Magnetic Measurement:

Variable-temperature (2.0 – 300 K) direct current (dc) magnetic susceptibility under an applied field of 1000 G where carried out with a Quantum Design SQUID magnetometer. The magnetic susceptibility data were corrected for the diamagnetism of the constituent atoms and the sample holder.

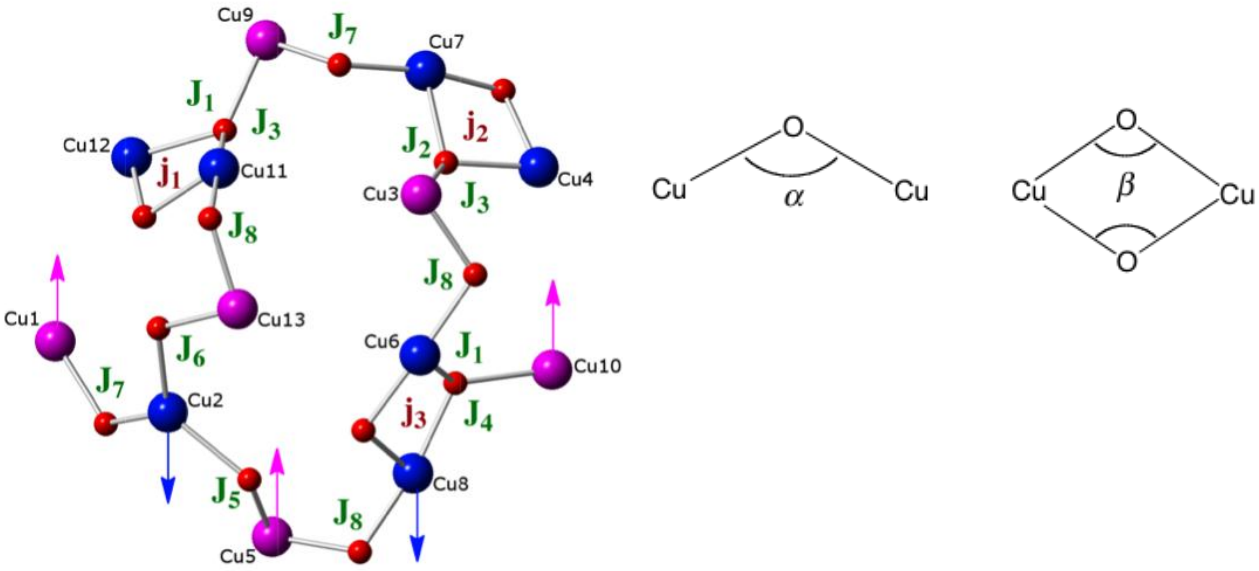


Fig. S9 Spin topology for a hemisphere of **1**. The Cu(II) with spin up and spin down are drawn in pink and blue colors, respectively. All the oxo-bridge (in red) pathways are shown and the corresponding angles at the bridge are indicated in the Tables below (an average angle is given for the double oxo-bridge).

parameter	J_1	J_2	J_3	J_4	J_5	J_6	J_7	J_8
α/ deg	126	124	122	121	117	115	114	112

parameter	j_1	j_2	j_3
β/ deg	96	97	98

Table S4. Details of the data collection and refinement parameters for **1.**

Identification code	**892148**
Empirical formula	$C_{206}H_{300}O_{68}P_{18}Cl_6Cu_{26}N_4$
Formula weight	6342.70
Temperature/K	173.15
Crystal system	monoclinic
Space group	C2/c
a/Å	39.396(3)
b/Å	23.230(3)
c/Å	39.059(5)
α/°	90.00
β/°	114.353(3)
γ/°	90.00
Volume/Å^3	32564(7)
Z	4
ρ_{calc}mg/mm^3	1.294
m/mm^{-1}	1.853
F(000)	12936.0
Crystal size/mm^3	0.35 × 0.25 × 0.1
2Θ range for data collection	3.68 to 50.54°
Index ranges	$-47 \leq h \leq 47$, $-27 \leq k \leq 24$, $-37 \leq l \leq 46$
Reflections collected	86350
Independent reflections	29481[R(int) = 0.0900]
Data/restraints/parameters	29481/492/1024
Goodness-of-fit on F^2	0.893
Final R indexes [I>=2σ (I)]	R_1 = 0.0734, wR_2 = 0.1875
Final R indexes [all data]	R_1 = 0.1201, wR_2 = 0.2085

Largest diff. peak/hole / e $Å^{-3}$	1.55/-1.27

Crystal Data: CCDC 892148 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S4. Bond lengths (Å) of **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	O2A	1.916(6)	C4A	C9A	1.362(15)
Cu1	O1B	1.916(5)	C5A	C6A	1.3900
Cu1	O3I	1.988(5)	C6A	C7A	1.3900
Cu1	O1HY	1.898(5)	C6A	C10A	1.595(15)
Cu2	O2B	2.125(5)	C7A	C2A	1.3900
Cu2	O3D	2.110(5)	C7A	C11A	1.478(15)
Cu2	O3I	2.118(5)	C1B	C2B	1.512(13)
Cu2	O2HY	1.957(5)	C2B	C3B	1.368(13)
Cu2	N2S	1.886(7)	C2B	C7B	1.396(13)
Cu3	Cu4	2.9497(14)	C3B	C4B	1.440(14)
Cu3	O1A	1.884(5)	C3B	C8B	1.562(12)
Cu3	O3B	1.956(5)	C4B	C5B	1.381(12)
Cu3	$O1F^{1}$	1.958(5)	C4B	C9B	1.535(13)
Cu3	$O6HY^{1}$	1.993(5)	C5B	C6B	1.421(13)
Cu3	N1	2.548(10)	C6B	C7B	1.355(14)

Cu4	O3B	1.974(5)	C6B	C10B	1.512(12)
Cu4	O2H^{1}	1.914(5)	C7B	C11B	1.525(13)
Cu4	O3HY	1.912(5)	C1C	C2C	1.494(10)
Cu4	O6HY^{1}	2.001(5)	C5C	C4C	1.3900
Cu5	O2B	1.993(5)	C5C	C6C	1.3900
Cu5	O1C	1.924(5)	C4C	C3C	1.3900
Cu5	O2D	1.912(5)	C4C	C9C	1.404(12)
Cu5	O3HY	1.904(5)	C3C	C2C	1.3900
Cu6	Cl3	2.682(2)	C3C	C8C	1.489(12)
Cu6	O3C	1.915(5)	C2C	C7C	1.3900
Cu6	O1E	1.956(5)	C7C	C6C	1.3900
Cu6	O3H^{1}	1.924(6)	C7C	C11C	1.545(13)
Cu6	O7HY^{1}	2.003(5)	C6C	C10C	1.590(12)
Cu7	Cu8	2.9761(15)	C1D	C2D	1.500(10)
Cu7	O2C	1.904(5)	C2D	C3D	1.391(11)
Cu7	O1D	1.938(5)	C2D	C7D	1.402(12)
Cu7	O1E	1.943(5)	C3D	C4D	1.403(11)
Cu7	O4HY	1.999(5)	C3D	C8D	1.538(12)
Cu8	Cl1	2.728(2)	C4D	C5D	1.376(13)
Cu8	O1D	1.988(5)	C4D	C9D	1.514(13)
Cu8	O2F	1.943(5)	C5D	C6D	1.433(13)
Cu8	O4HY	1.988(5)	C6D	C7D	1.377(12)

Cu8	O5HY	1.894(5)	C6D	C10D	1.500(12)
Cu9	Cl2	2.695(2)	C7D	C11D	1.526(12)
Cu9	O3A^{1}	1.918(5)	O2E	Cu13^{1}	1.930(5)
Cu9	O3E	1.910(5)	C1E	C2E	1.542(12)
Cu9	O1F	1.980(5)	C2E	C3E	1.413(16)
Cu9	O4HY	2.021(5)	C2E	C7E	1.404(15)
Cu10	O3D	1.982(5)	C3E	C4E	1.425(13)
Cu10	O2G	1.919(5)	C3E	C8E	1.466(15)
Cu10	O2I	1.935(5)	C4E	C5E	1.382(15)
Cu10	O5HY	1.907(5)	C4E	C9E	1.528(15)
Cu11	Cl1	2.644(2)	C5E	C6E	1.337(15)
Cu11	O3F	1.900(6)	C6E	C7E	1.386(13)
Cu11	O3G	1.938(5)	C6E	C10E	1.533(15)
Cu11	O1H	1.952(5)	C7E	C11E	1.505(15)
Cu11	O6HY	2.014(5)	O1F	Cu3^{1}	1.958(5)
Cu12	Cu13	2.9559(14)	C1F	C2F	1.509(13)
Cu12	O1G	1.890(5)	C3F	C4F	1.3900
Cu12	O1H	1.938(5)	C3F	C2F	1.3900
Cu12	O1I	1.944(5)	C3F	C8F	1.503(14)
Cu12	O7HY	2.001(5)	C4F	C5F	1.3900
Cu13	Cl2^{1}	2.746(2)	C4F	C9F	1.483(13)
Cu13	O2E^{1}	1.930(5)	C5F	C6F	1.3900

Cu13	O1I	1.973(5)	C6F	C7F	1.3900
Cu13	O1HY	1.896(5)	C6F	C10F	1.616(14)
Cu13	O7HY	1.992(5)	C7F	C2F	1.3900
Cl2	Cu13[1]	2.746(2)	C7F	C11F	1.516(13)
P1	O1A	1.530(6)	C1G	C2G	1.538(12)
P1	O2A	1.517(6)	C2G	C3G	1.417(13)
P1	O3A	1.516(6)	C2G	C7G	1.356(13)
P1	C1A	1.850(8)	C3G	C4G	1.385(13)
P2	O1B	1.493(5)	C3G	C8G	1.476(14)
P2	O2B	1.535(5)	C4G	C5G	1.367(14)
P2	O3B	1.549(5)	C4G	C9G	1.532(13)
P2	C1B	1.779(10)	C5G	C6G	1.408(13)
P3	O1C	1.528(5)	C6G	C7G	1.425(12)
P3	O2C	1.499(6)	C6G	C10G	1.490(14)
P3	O3C	1.541(6)	C7G	C11G	1.523(13)
P3	C1C	1.850(9)	O2H	Cu4[1]	1.914(5)
P4	O1D	1.555(5)	O3H	Cu6[1]	1.924(6)
P4	O2D	1.493(5)	C1H	C2H	1.513(13)
P4	O3D	1.543(5)	C3H	C4H	1.3900
P4	C1D	1.794(7)	C3H	C2H	1.3900
P5	O1E	1.560(5)	C3H	C8H	1.450(14)
P5	O2E	1.499(6)	C4H	C5H	1.3900

P5	O3E	1.532(6)	C4H	C9H	1.437(13)
P5	C1E	1.807(9)	C5H	C6H	1.3900
P6	O1F	1.533(5)	C6H	C7H	1.3900
P6	O2F	1.502(5)	C6H	C10H	1.555(14)
P6	O3F	1.524(6)	C7H	C2H	1.3900
P6	C1F	1.805(12)	C7H	C11H	1.483(14)
P7	O1G	1.520(6)	C1I	C2I	1.513(15)
P7	O2G	1.530(6)	C2I	C3I	1.366(17)
P7	O3G	1.537(6)	C2I	C7I	1.375(16)
P7	C1G	1.818(8)	C3I	C4I	1.359(15)
P8	O1H	1.564(5)	C3I	C8I	1.513(16)
P8	O2H	1.525(5)	C4I	C5I	1.321(15)
P8	O3H	1.495(6)	C4I	C9I	1.530(16)
P8	C1H	1.816(12)	C5I	C6I	1.363(16)
P9	O1I	1.558(5)	C6I	C7I	1.424(15)
P9	O2I	1.475(5)	C6I	C10I	1.596(16)
P9	O3I	1.534(5)	C7I	C11I	1.570(16)
P9	C1I	1.769(13)	O6HY	$Cu3^{1}$	1.993(5)
O3A	$Cu9^{1}$	1.918(5)	O6HY	$Cu4^{1}$	2.001(5)
C1A	C2A	1.541(12)	O7HY	$Cu6^{1}$	2.003(5)
C3A	C4A	1.3900	N2S	C21S	1.171(12)
C3A	C2A	1.3900	C21S	C22S	1.511(12)

C3A	C8A	1.396(12)	N1	C8	1.38(2)
C4A	C5A	1.3900	C7	C8	1.549(16)

Table S3. Bond angle (°) of **1**.

Table 5 Bond Angles for cu26-sr.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2A	Cu1	O1B	95.2(2)	C7A	C6A	C10A	127.7(11)
O2A	Cu1	O3I	167.0(2)	C6A	C7A	C11A	109.2(12)
O1B	Cu1	O3I	86.5(2)	C2A	C7A	C6A	120.0
O1HY	Cu1	O2A	87.8(2)	C2A	C7A	C11A	130.7(12)
O1HY	Cu1	O1B	176.9(2)	C3A	C2A	C1A	128.1(11)
O1HY	Cu1	O3I	90.5(2)	C7A	C2A	C1A	111.9(11)
O3D	Cu2	O2B	120.04(19)	C7A	C2A	C3A	120.0
O3D	Cu2	O3I	118.4(2)	P2	O1B	Cu1	149.3(3)
O3I	Cu2	O2B	120.83(19)	Cu5	O2B	Cu2	114.9(2)
O2HY	Cu2	O2B	88.22(19)	P2	O2B	Cu2	109.2(3)

O2HY	Cu2	O3D	86.4(2)	P2	O2B	Cu5	129.3(3)
O2HY	Cu2	O3I	86.8(2)	Cu3	O3B	Cu4	97.3(2)
N2S	Cu2	O2B	93.5(3)	P2	O3B	Cu3	133.9(3)
N2S	Cu2	O3D	94.3(2)	P2	O3B	Cu4	128.6(3)
N2S	Cu2	O3I	90.9(3)	C2B	C1B	P2	116.7(9)
N2S	Cu2	O2HY	177.6(3)	C3B	C2B	C1B	120.2(9)
O1A	Cu3	Cu4	129.73(16)	C3B	C2B	C7B	119.6(10)
O1A	Cu3	O3B	96.3(2)	C7B	C2B	C1B	120.0(9)
O1A	Cu3	O1F^{1}	93.5(2)	C2B	C3B	C4B	120.7(9)
O1A	Cu3	O6HY^{1}	166.7(2)	C2B	C3B	C8B	123.1(9)
O1A	Cu3	N1	87.6(3)	C4B	C3B	C8B	115.8(9)
O3B	Cu3	Cu4	41.58(14)	C3B	C4B	C9B	123.2(8)
O3B	Cu3	O1F^{1}	165.6(2)	C5B	C4B	C3B	117.6(10)
O3B	Cu3	O6HY^{1}	80.9(2)	C5B	C4B	C9B	119.2(10)
O3B	Cu3	N1	84.1(3)	C4B	C5B	C6B	121.1(10)
O1F^{1}	Cu3	Cu4	134.09(15)	C5B	C6B	C10B	116.7(9)
O1F^{1}	Cu3	O6HY^{1}	91.9(2)	C7B	C6B	C5B	119.1(9)
O1F^{1}	Cu3	N1	107.0(3)	C7B	C6B	C10B	124.0(9)
O6HY^{1}	Cu3	Cu4	42.49(14)	C2B	C7B	C11B	119.7(9)
O6HY^{1}	Cu3	N1	79.2(3)	C6B	C7B	C2B	121.7(10)
N1	Cu3	Cu4	66.4(2)	C6B	C7B	C11B	118.6(9)
O3B	Cu4	Cu3	41.12(15)	P3	O1C	Cu5	127.3(3)

O3B	Cu4	O6HY^{1}	80.3(2)	P3	O2C	Cu7	127.9(3)
O2H^{1}	Cu4	Cu3	125.71(17)	P3	O3C	Cu6	130.2(3)
O2H^{1}	Cu4	O3B	158.2(2)	C2C	C1C	P3	116.2(6)
O2H^{1}	Cu4	O6HY^{1}	95.7(2)	C4C	C5C	C6C	120.0
O3HY	Cu4	Cu3	131.97(15)	C5C	C4C	C3C	120.0
O3HY	Cu4	O3B	92.1(2)	C5C	C4C	C9C	114.1(7)
O3HY	Cu4	O2H^{1}	93.6(2)	C3C	C4C	C9C	125.8(7)
O3HY	Cu4	O6HY^{1}	170.2(2)	C4C	C3C	C8C	118.2(7)
O6HY^{1}	Cu4	Cu3	42.28(13)	C2C	C3C	C4C	120.0
O1C	Cu5	O2B	164.7(2)	C2C	C3C	C8C	121.7(7)
O2D	Cu5	O2B	85.9(2)	C3C	C2C	C1C	118.9(8)
O2D	Cu5	O1C	92.0(2)	C7C	C2C	C1C	121.1(8)
O3HY	Cu5	O2B	91.1(2)	C7C	C2C	C3C	120.0
O3HY	Cu5	O1C	90.5(2)	C2C	C7C	C6C	120.0
O3HY	Cu5	O2D	176.8(2)	C2C	C7C	C11C	121.1(7)
O3C	Cu6	Cl3	96.74(16)	C6C	C7C	C11C	118.9(7)
O3C	Cu6	O1E	91.2(2)	C5C	C6C	C10C	120.5(7)
O3C	Cu6	O3H^{1}	90.5(2)	C7C	C6C	C5C	120.0
O3C	Cu6	O7HY^{1}	178.0(2)	C7C	C6C	C10C	119.5(7)
O1E	Cu6	Cl3	85.16(15)	Cu7	O1D	Cu8	98.6(2)
O1E	Cu6	O7HY^{1}	87.2(2)	P4	O1D	Cu7	133.4(3)
O3H^{1}	Cu6	Cl3	109.73(17)	P4	O1D	Cu8	128.0(3)

O3H[1]	Cu6	O1E	164.7(2)	P4	O2D	Cu5	149.6(3)
O3H[1]	Cu6	O7HY[1]	90.7(2)	Cu10	O3D	Cu2	116.5(2)
O7HY[1]	Cu6	Cl3	84.42(14)	P4	O3D	Cu2	109.9(3)
O2C	Cu7	Cu8	127.96(17)	P4	O3D	Cu10	129.0(3)
O2C	Cu7	O1D	95.4(2)	C2D	C1D	P4	114.2(5)
O2C	Cu7	O1E	91.5(2)	C3D	C2D	C1D	121.3(8)
O2C	Cu7	O4HY	160.7(2)	C3D	C2D	C7D	120.5(7)
O1D	Cu7	Cu8	41.34(15)	C7D	C2D	C1D	118.2(8)
O1D	Cu7	O1E	172.0(2)	C2D	C3D	C4D	118.9(8)
O1D	Cu7	O4HY	81.0(2)	C2D	C3D	C8D	124.2(7)
O1E	Cu7	Cu8	134.86(15)	C4D	C3D	C8D	116.9(8)
O1E	Cu7	O4HY	93.9(2)	C3D	C4D	C9D	121.6(9)
O4HY	Cu7	Cu8	41.59(14)	C5D	C4D	C3D	120.7(9)
Cl1	Cu8	Cu7	105.28(6)	C5D	C4D	C9D	117.7(9)
O1D	Cu8	Cu7	40.07(15)	C4D	C5D	C6D	120.7(9)
O1D	Cu8	Cl1	99.43(15)	C5D	C6D	C10D	119.3(9)
O1D	Cu8	O4HY	80.0(2)	C7D	C6D	C5D	117.8(9)
O2F	Cu8	Cu7	124.55(17)	C7D	C6D	C10D	122.9(10)
O2F	Cu8	Cl1	107.52(16)	C2D	C7D	C11D	121.0(7)
O2F	Cu8	O1D	152.7(2)	C6D	C7D	C2D	121.4(9)
O2F	Cu8	O4HY	95.5(2)	C6D	C7D	C11D	117.6(9)
O4HY	Cu8	Cu7	41.85(14)	Cu7	O1E	Cu6	112.1(2)

O4HY	Cu8	Cl1	89.23(15)	P5	O1E	Cu6	124.7(3)
O5HY	Cu8	Cu7	130.42(16)	P5	O1E	Cu7	122.7(3)
O5HY	Cu8	Cl1	87.99(16)	P5	O2E	Cu13[1]	127.0(3)
O5HY	Cu8	O1D	91.2(2)	P5	O3E	Cu9	125.3(3)
O5HY	Cu8	O2F	94.3(2)	C2E	C1E	P5	115.9(7)
O5HY	Cu8	O4HY	170.2(2)	C3E	C2E	C1E	119.0(11)
O3A[1]	Cu9	Cl2	97.87(18)	C7E	C2E	C1E	118.8(11)
O3A[1]	Cu9	O1F	91.0(2)	C7E	C2E	C3E	122.1(10)
O3A[1]	Cu9	O4HY	178.9(2)	C2E	C3E	C4E	117.4(11)
O3E	Cu9	Cl2	110.95(18)	C2E	C3E	C8E	122.9(9)
O3E	Cu9	O3A[1]	91.3(2)	C4E	C3E	C8E	119.6(11)
O3E	Cu9	O1F	162.3(2)	C3E	C4E	C9E	120.5(11)
O3E	Cu9	O4HY	89.4(2)	C5E	C4E	C3E	117.4(12)
O1F	Cu9	Cl2	86.12(15)	C5E	C4E	C9E	122.1(9)
O1F	Cu9	O4HY	88.0(2)	C6E	C5E	C4E	125.0(10)
O4HY	Cu9	Cl2	82.64(15)	C5E	C6E	C7E	119.6(12)
O2G	Cu10	O3D	166.1(2)	C5E	C6E	C10E	120.9(9)
O2G	Cu10	O2I	92.2(2)	C7E	C6E	C10E	119.3(12)
O2I	Cu10	O3D	86.5(2)	C2E	C7E	C11E	120.1(9)
O5HY	Cu10	O3D	91.0(2)	C6E	C7E	C2E	118.2(12)
O5HY	Cu10	O2G	89.6(2)	C6E	C7E	C11E	121.5(11)
O5HY	Cu10	O2I	176.5(2)	Cu3[1]	O1F	Cu9	113.7(3)

O3F	Cu11	Cl1	108.95(17)	P6	O1F	Cu3[1]	123.2(3)
O3F	Cu11	O3G	88.4(2)	P6	O1F	Cu9	122.2(3)
O3F	Cu11	O1H	165.3(2)	P6	O2F	Cu8	123.9(3)
O3F	Cu11	O6HY	91.5(2)	P6	O3F	Cu11	127.6(3)
O3G	Cu11	Cl1	97.44(16)	C2F	C1F	P6	115.1(9)
O3G	Cu11	O1H	90.8(2)	C4F	C3F	C2F	120.0
O3G	Cu11	O6HY	177.0(2)	C4F	C3F	C8F	120.3(9)
O1H	Cu11	Cl1	85.67(15)	C2F	C3F	C8F	119.7(9)
O1H	Cu11	O6HY	88.6(2)	C3F	C4F	C5F	120.0
O6HY	Cu11	Cl1	85.42(15)	C3F	C4F	C9F	124.7(9)
O1G	Cu12	Cu13	128.11(17)	C5F	C4F	C9F	115.3(9)
O1G	Cu12	O1H	92.1(2)	C6F	C5F	C4F	120.0
O1G	Cu12	O1I	95.9(2)	C5F	C6F	C7F	120.0
O1G	Cu12	O7HY	161.3(2)	C5F	C6F	C10F	120.5(8)
O1H	Cu12	Cu13	135.33(15)	C7F	C6F	C10F	119.5(8)
O1H	Cu12	O1I	168.9(2)	C6F	C7F	C2F	120.0
O1H	Cu12	O7HY	93.5(2)	C6F	C7F	C11F	118.0(9)
O1I	Cu12	Cu13	41.37(14)	C2F	C7F	C11F	122.0(9)
O1I	Cu12	O7HY	81.3(2)	C3F	C2F	C1F	120.3(9)
O7HY	Cu12	Cu13	42.14(14)	C7F	C2F	C1F	119.7(9)
Cl2[1]	Cu13	Cu12	105.06(5)	C7F	C2F	C3F	120.0
O2E[1]	Cu13	Cu12	127.81(17)	P7	O1G	Cu12	128.3(3)

O2E[1]	Cu13	Cl2[1]	104.30(18)	P7	O2G	Cu10	127.5(3)
O2E[1]	Cu13	O1I	158.2(2)	P7	O3G	Cu11	129.6(3)
O2E[1]	Cu13	O7HY	96.4(2)	C2G	C1G	P7	117.4(6)
O1I	Cu13	Cu12	40.65(14)	C3G	C2G	C1G	118.6(9)
O1I	Cu13	Cl2[1]	97.36(14)	C7G	C2G	C1G	119.8(9)
O1I	Cu13	O7HY	80.8(2)	C7G	C2G	C3G	121.6(9)
O1HY	Cu13	Cu12	130.41(18)	C2G	C3G	C8G	120.7(9)
O1HY	Cu13	Cl2[1]	88.53(18)	C4G	C3G	C2G	117.8(10)
O1HY	Cu13	O2E[1]	92.3(2)	C4G	C3G	C8G	121.5(10)
O1HY	Cu13	O1I	91.1(2)	C3G	C4G	C9G	123.7(11)
O1HY	Cu13	O7HY	171.3(2)	C5G	C4G	C3G	121.7(10)
O7HY	Cu13	Cu12	42.37(14)	C5G	C4G	C9G	114.6(10)
O7HY	Cu13	Cl2[1]	89.56(15)	C4G	C5G	C6G	120.8(10)
Cu11	Cl1	Cu8	97.28(7)	C5G	C6G	C7G	117.8(10)
Cu9	Cl2	Cu13[1]	96.78(7)	C5G	C6G	C10G	120.0(9)
O1A	P1	C1A	107.1(4)	C7G	C6G	C10G	122.2(9)
O2A	P1	O1A	112.8(3)	C2G	C7G	C6G	120.3(9)
O2A	P1	C1A	103.8(4)	C2G	C7G	C11G	120.6(9)
O3A	P1	O1A	112.9(3)	C6G	C7G	C11G	119.1(9)
O3A	P1	O2A	112.7(3)	Cu12	O1H	Cu11	113.5(2)
O3A	P1	C1A	106.7(4)	P8	O1H	Cu11	123.2(3)
O1B	P2	O2B	109.8(3)	P8	O1H	Cu12	122.7(3)

O1B	P2	O3B	113.4(3)	P8	O2H	Cu4[1]	126.5(3)
O1B	P2	C1B	108.4(4)	P8	O3H	Cu6[1]	127.1(3)
O2B	P2	O3B	108.5(3)	C2H	C1H	P8	112.6(9)
O2B	P2	C1B	109.3(4)	C4H	C3H	C2H	120.0
O3B	P2	C1B	107.4(4)	C4H	C3H	C8H	119.0(9)
O1C	P3	O3C	112.3(3)	C2H	C3H	C8H	120.9(9)
O1C	P3	C1C	103.2(4)	C3H	C4H	C5H	120.0
O2C	P3	O1C	112.5(3)	C3H	C4H	C9H	126.6(9)
O2C	P3	O3C	112.5(3)	C5H	C4H	C9H	113.2(9)
O2C	P3	C1C	108.7(5)	C6H	C5H	C4H	120.0
O3C	P3	C1C	107.1(4)	C5H	C6H	C7H	120.0
O1D	P4	C1D	107.5(3)	C5H	C6H	C10H	118.6(9)
O2D	P4	O1D	113.0(3)	C7H	C6H	C10H	121.3(9)
O2D	P4	O3D	110.1(3)	C6H	C7H	C2H	120.0
O2D	P4	C1D	107.9(3)	C6H	C7H	C11H	117.6(9)
O3D	P4	O1D	108.0(3)	C2H	C7H	C11H	122.3(9)
O3D	P4	C1D	110.3(3)	C3H	C2H	C1H	118.5(9)
O1E	P5	C1E	105.8(4)	C7H	C2H	C1H	121.3(9)
O2E	P5	O1E	108.6(3)	C7H	C2H	C3H	120.0
O2E	P5	O3E	116.3(3)	Cu12	O1I	Cu13	98.0(2)
O2E	P5	C1E	108.8(4)	P9	O1I	Cu12	133.3(3)
O3E	P5	O1E	108.6(3)	P9	O1I	Cu13	128.4(3)

O3E	P5	C1E	108.4(5)	P9	O2I	Cu10	146.9(3)
O1F	P6	C1F	106.9(5)	Cu1	O3I	Cu2	114.2(3)
O2F	P6	O1F	108.9(3)	P9	O3I	Cu1	129.0(3)
O2F	P6	O3F	115.4(3)	P9	O3I	Cu2	110.8(3)
O2F	P6	C1F	109.1(5)	C2I	C1I	P9	118.1(10)
O3F	P6	O1F	109.4(3)	C3I	C2I	C1I	120.1(12)
O3F	P6	C1F	106.9(5)	C3I	C2I	C7I	119.4(12)
O1G	P7	O2G	111.9(3)	C7I	C2I	C1I	120.5(12)
O1G	P7	O3G	113.1(3)	C2I	C3I	C8I	121.5(11)
O1G	P7	C1G	108.9(4)	C4I	C3I	C2I	122.5(13)
O2G	P7	O3G	111.2(3)	C4I	C3I	C8I	115.9(12)
O2G	P7	C1G	103.5(4)	C3I	C4I	C9I	125.7(12)
O3G	P7	C1G	107.6(4)	C5I	C4I	C3I	118.4(13)
O1H	P8	C1H	105.9(5)	C5I	C4I	C9I	115.2(11)
O2H	P8	O1H	108.7(3)	C4I	C5I	C6I	122.2(12)
O2H	P8	C1H	106.8(5)	C5I	C6I	C7I	119.5(12)
O3H	P8	O1H	110.0(3)	C5I	C6I	C10I	122.6(11)
O3H	P8	O2H	115.8(3)	C7I	C6I	C10I	117.6(12)
O3H	P8	C1H	109.2(5)	C2I	C7I	C6I	117.0(13)
O1I	P9	C1I	106.4(4)	C2I	C7I	C11I	123.9(11)
O2I	P9	O1I	113.0(3)	C6I	C7I	C11I	119.0(11)
O2I	P9	O3I	110.4(3)	Cu13	O1HY	Cu1	112.8(2)

O2I	P9	C1I	107.2(5)	Cu5	O3HY	Cu4	112.2(2)
O3I	P9	O1I	107.2(3)	Cu7	O4HY	Cu9	124.7(2)
O3I	P9	C1I	112.7(5)	Cu8	O4HY	Cu7	96.6(2)
P1	O1A	Cu3	128.4(3)	Cu8	O4HY	Cu9	120.9(2)
P1	O2A	Cu1	128.3(3)	Cu8	O5HY	Cu10	111.8(2)
P1	O3A	Cu9[1]	130.3(3)	Cu3[1]	O6HY	Cu4[1]	95.2(2)
C2A	C1A	P1	117.0(6)	Cu3[1]	O6HY	Cu11	124.8(2)
C4A	C3A	C2A	120.0	Cu4[1]	O6HY	Cu11	122.2(2)
C4A	C3A	C8A	130.7(12)	Cu12	O7HY	Cu6[1]	125.2(2)
C2A	C3A	C8A	109.3(12)	Cu13	O7HY	Cu6[1]	123.3(2)
C5A	C4A	C3A	120.0	Cu13	O7HY	Cu12	95.5(2)
C9A	C4A	C3A	123.5(12)	C21S	N2S	Cu2	175.0(9)
C9A	C4A	C5A	116.0(13)	N2S	C21S	C22S	174.7(14)
C4A	C5A	C6A	120.0	C8	N1	Cu3	154.2(12)
C5A	C6A	C10A	112.3(11)	N1	C8	C7	172(2)
C7A	C6A	C5A	120.0				

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,-y+1/2,-z+1