Electronic Supplementary Information (ESI)

A Hexadecameric Copper(II) Phosphonate Cage

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Experimental section.

ESI-MS spectra were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. The following ionization protocols were used *: electro spray in both positive and negative ion full scan mode* using acetonitrile/formic acid (80:20% and 0.1% water) as solvent and nitrogen gas for desolvation. For negative ion mode, capillary voltage was maintained at 3 kV and cone voltage was kept at 31.0 V and for positive ion mode capillary voltage and cone voltage was maintained at 2.8 kV and 32 V respectively. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT IR spectrophotometer operating from 400-4000 cm^{-1}. Thermo Gravimetric Analysis was carried out on a Perkin Elmer Pyris 6 Thermogravimetric Analyzer. Magnetic susceptibility measurements of **1** were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. Measurements were performed on finely ground crystalline sample of 7.0 mg. The magnetic data were corrected for the sample holder and the diamagnetic contribution.

X-ray crystallography.

Single-crystal X-ray structural studies of **1** was performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 153(2) K using graphite-monochromated Mo Kα radiation (λ_α= 0.71069 Å). The crystals did not decompose during data collection. Data collection, structure solution and refinement were performed using SMART,[a] SAINT[b] and SHELXTL[c-d] programs respectively. All calculations for data reduction were done using the Bruker SADABS[e] program. All the non-hydrogen atoms of **1** were refined anisotropically using full-matrix least-square method. All the hydrogen atoms of **1** except the O-H hydroxides were included in idealized positions, and a riding model was used. The hydrogen atoms of hydroxide were added from difference Fourier map. All the H-bonding interactions and molecular drawings were obtained from DIAMOND 3.1f package.[f] The bonding parameters were obtained from WINGX 1.70.01[g-h] crystallographic collective package. The carbon and oxygen atoms of ethyl acetate solvent molecule are having high thermal parameter and so refined isotropically. Therefore, this solvent molecule is then

squeezed out using SQUEEZE program in WINGX package 1.70.01. The total potential solvent accessible void volume is found to be 386.6 $Å^3$ and the electron count /cell = 90. As since the acetonitirle solvent molecule coordinates to the copper centres in different asymmetric unit, it has been moved near to the same asymmetric unit using MOVE command in SHELXTL package.

(a) SMART Software Reference Manual Bruker-AXS, 6300 Enterprise Dr. Madison, WI 53719-1173, USA, 1994.

(b) SAINT Software Reference Manual Bruker-AXS, 6300 Enterprise Dr. Madison, WI 53719-1173, USA, 1995.

(c) Sheldrick, G. M. SHELXTL, Version 5 Reference Manual, Bruker-AXS, 6300 Enterprise Dr. Madison, WI 53719-1173, USA, 1994.

(d) SHELXTL-PC Package, Bruker Analytical X-ray Systems, Madison, WI, **1998**.

(e) Sheldrick, G. M. SADABS, Universität Göttingen, Germany, 1996. Bruker Analytical X-ray Systems, Madison, WI, **2001**.

(f) DIAMOND version 3.1f, Crystal Impact GbR, Bonn, Germany, **2004**.

(g) Farrugia, L. J. Department of Chemistry, University of Glasgow (1997-2005), WinGX, Version 1.70.01a; An integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-Ray Diffraction Data.

(h) Farrugia, L. J. *J. Appl. Cryst*. **1999**, *32*, 837.

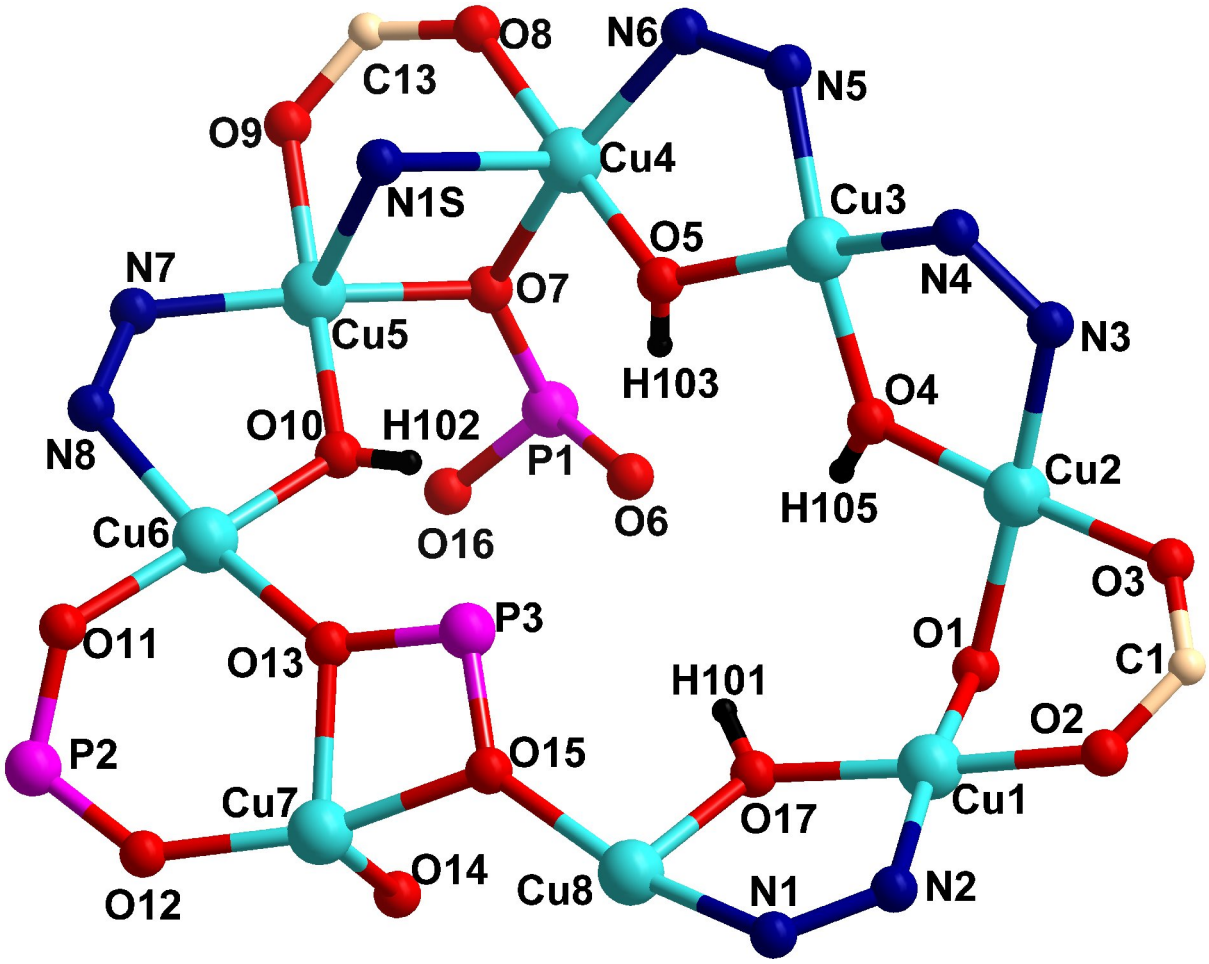


Figure S1. Asymmetric unit contents of **1**. Carbon atoms of the phosphonate, pyrazole and acetonitrile ligands have been removed for clarity.

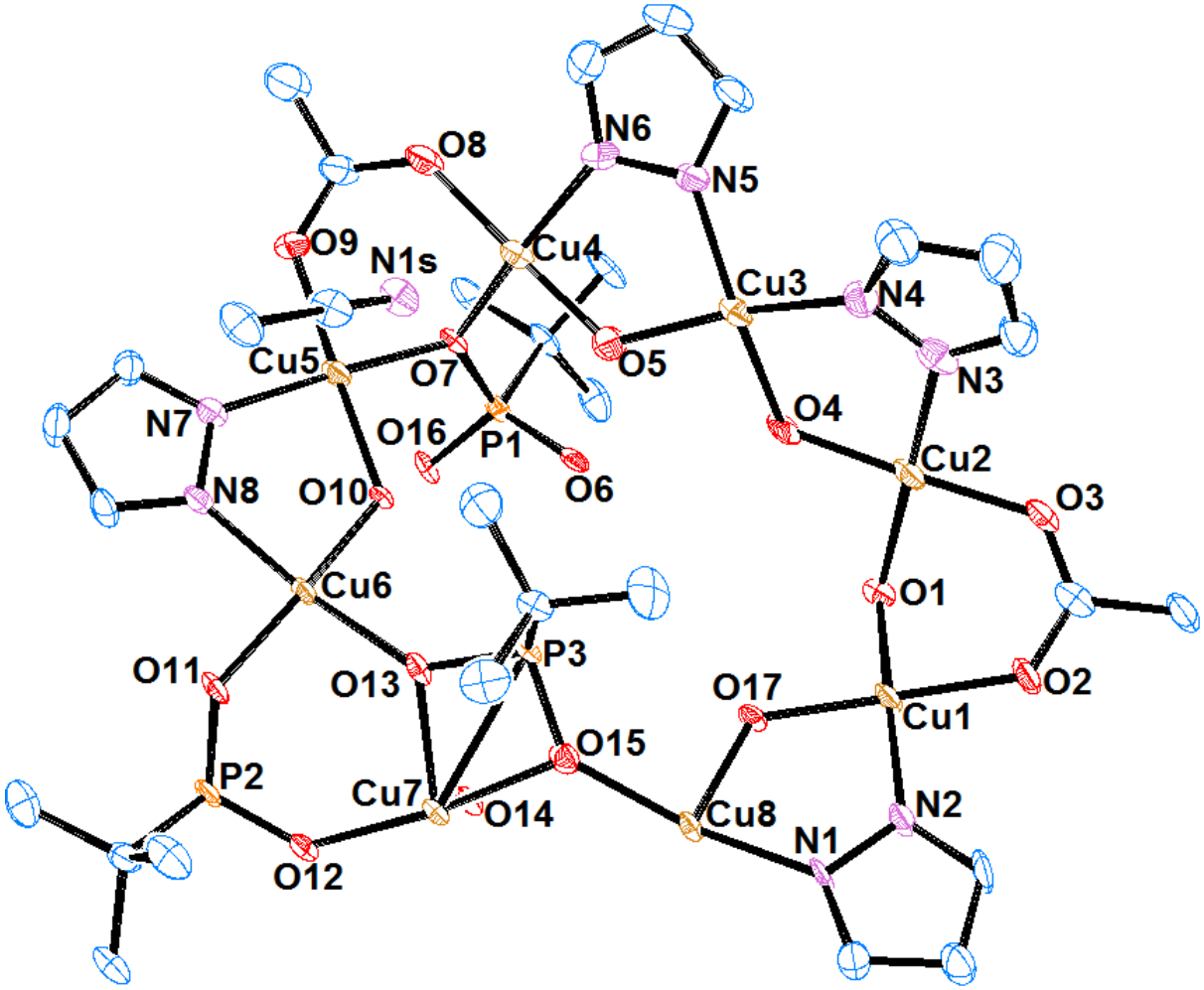


Figure S2. ORTEP diagram of **1** with 50 % thermal ellipsoids (asymmetric unit).

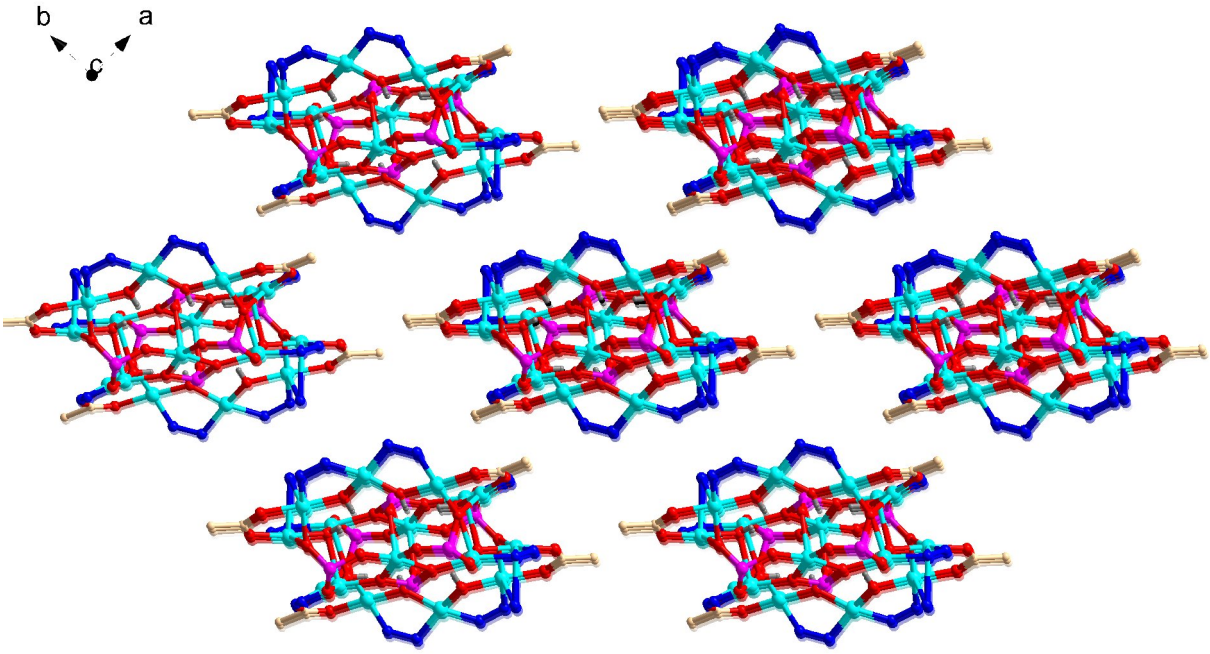


Figure S3. Packing diagram of **1**. View along 'c' axis. Each molecule of **1** is surrounded by six other similar Cu_{16} cages.

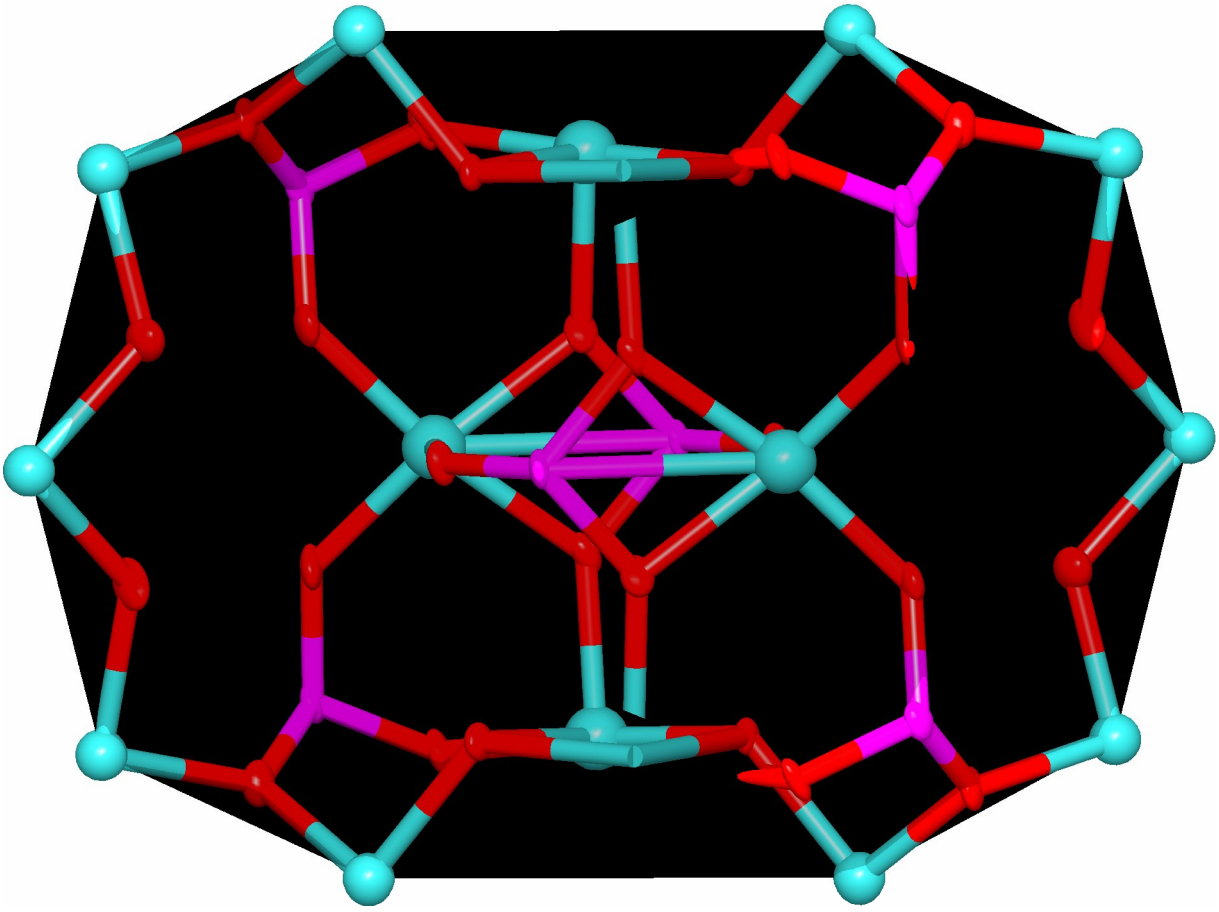


Figure S4. View showing the ellipsoidal shape of **1**.

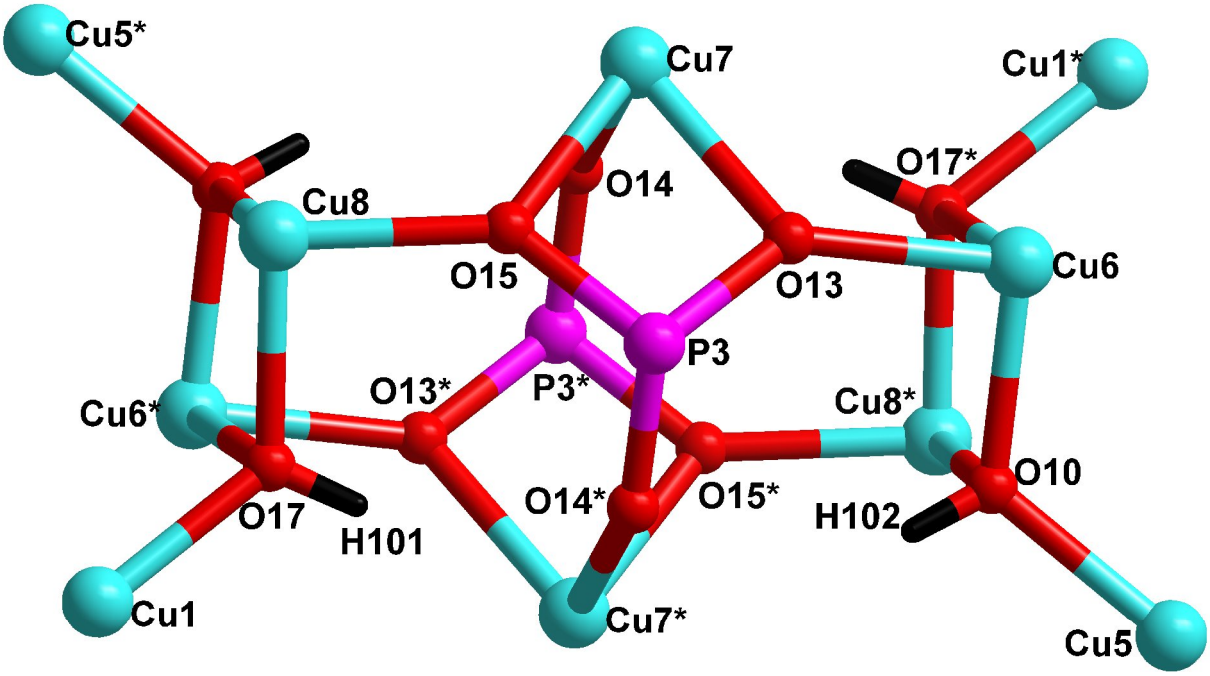


Figure S5. View of inner decacopper core showing the ellipsoidal void contained in the cage **1**. The dimensions of this void may be gauged by the following distances: inter-planar distance between the two $Cu_2[\mu_3\text{-}OH]_2$ four-membered rings in the *wings*, 6.18 Å; distance between the two *rim* copper atoms (Cu7 and Cu7*), 4.83 Å; distance between the *rim* phosphorus atoms (P3 and P3*), 3.91 Å and distance between the *rim* oxygen atoms (O13 and O13*), 3.92 Å.

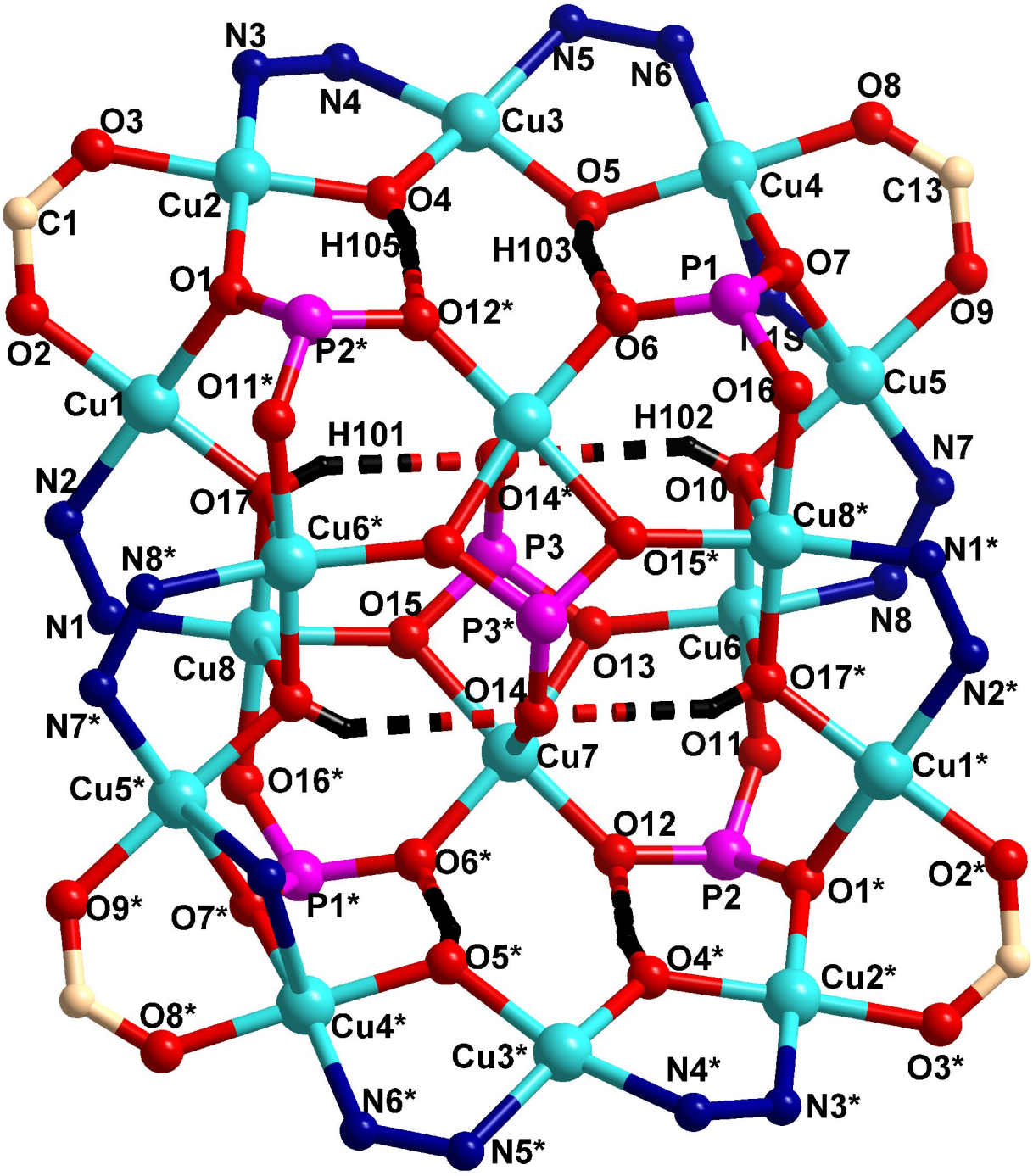


Figure S6. Molecular structure of **1**. Carbon atoms of pyrazole, acetonitrile, phosphonic acid and acetate ligands have been removed for clarity.

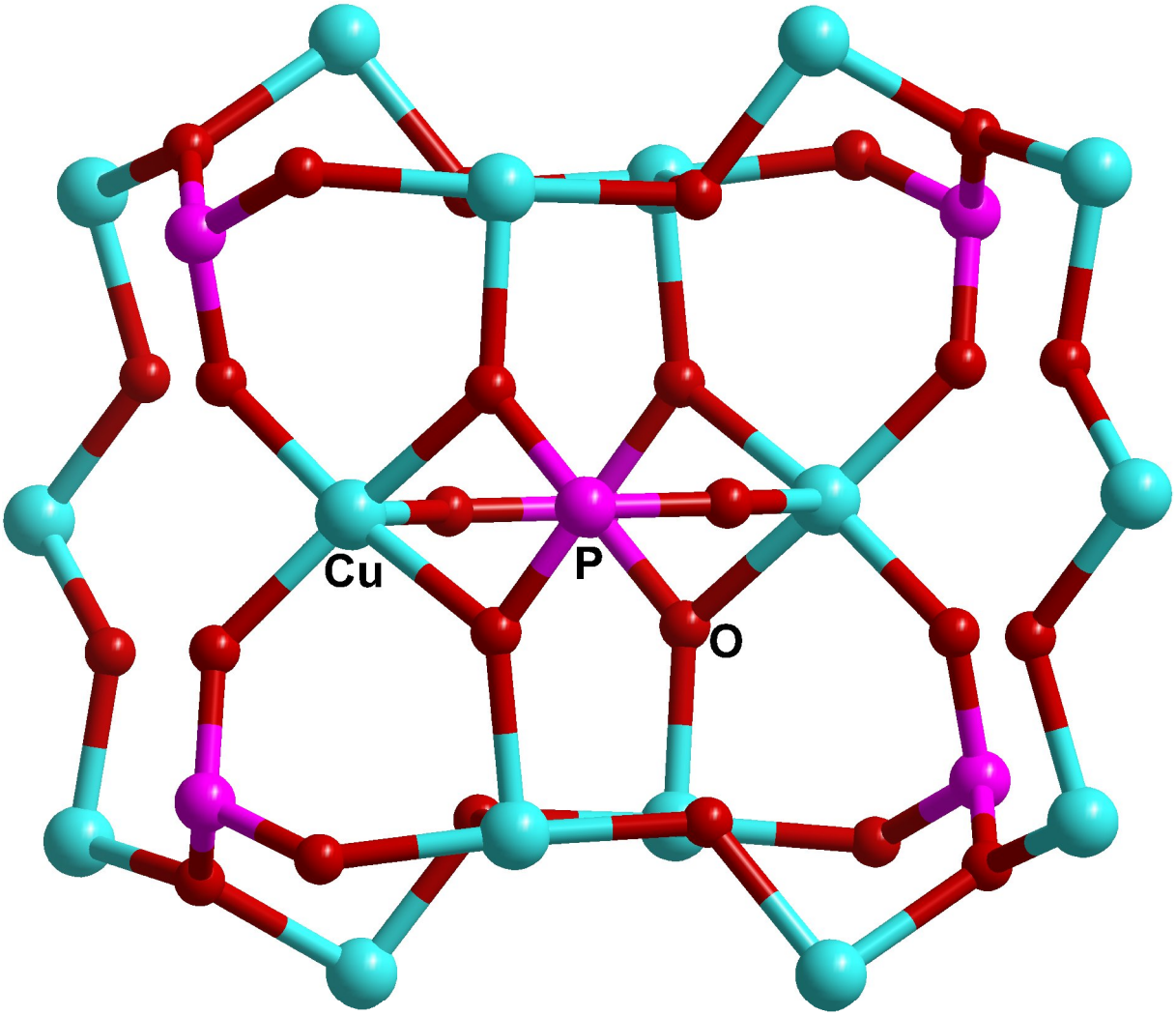


Figure S7. Core structure of **1** showing the presence of several ring systems in the cage (See Table S3 for details).

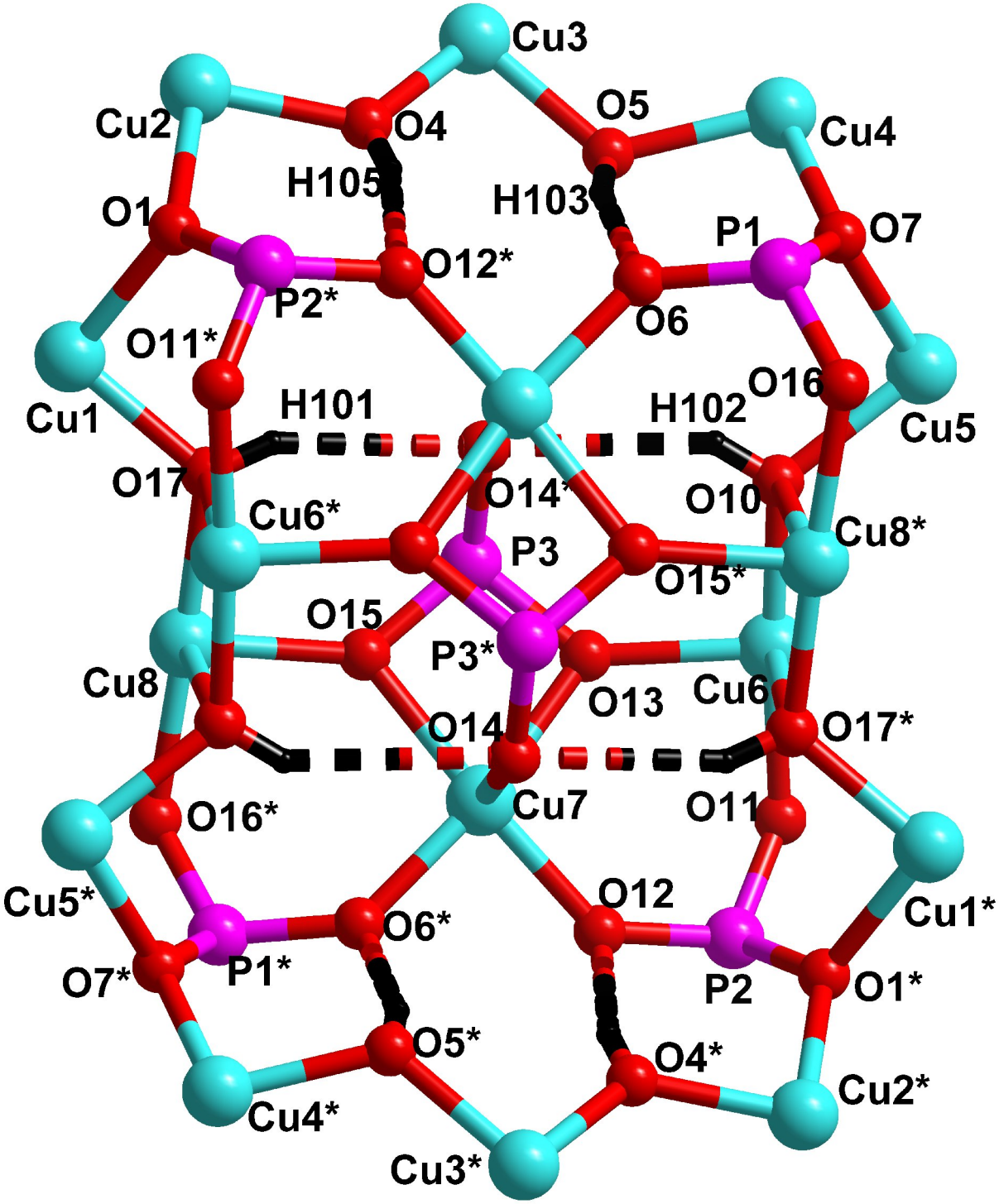


Figure S8. Core structure of **1** showing the presence of various intramolecular O-H···O interactions. The bond parameters are: O17-H101···O14 2.467(8); O10-H102···O14 2.315(6); O5-H103···O6 2.203(3); O4-H105···O12* 2.133(4) Å.

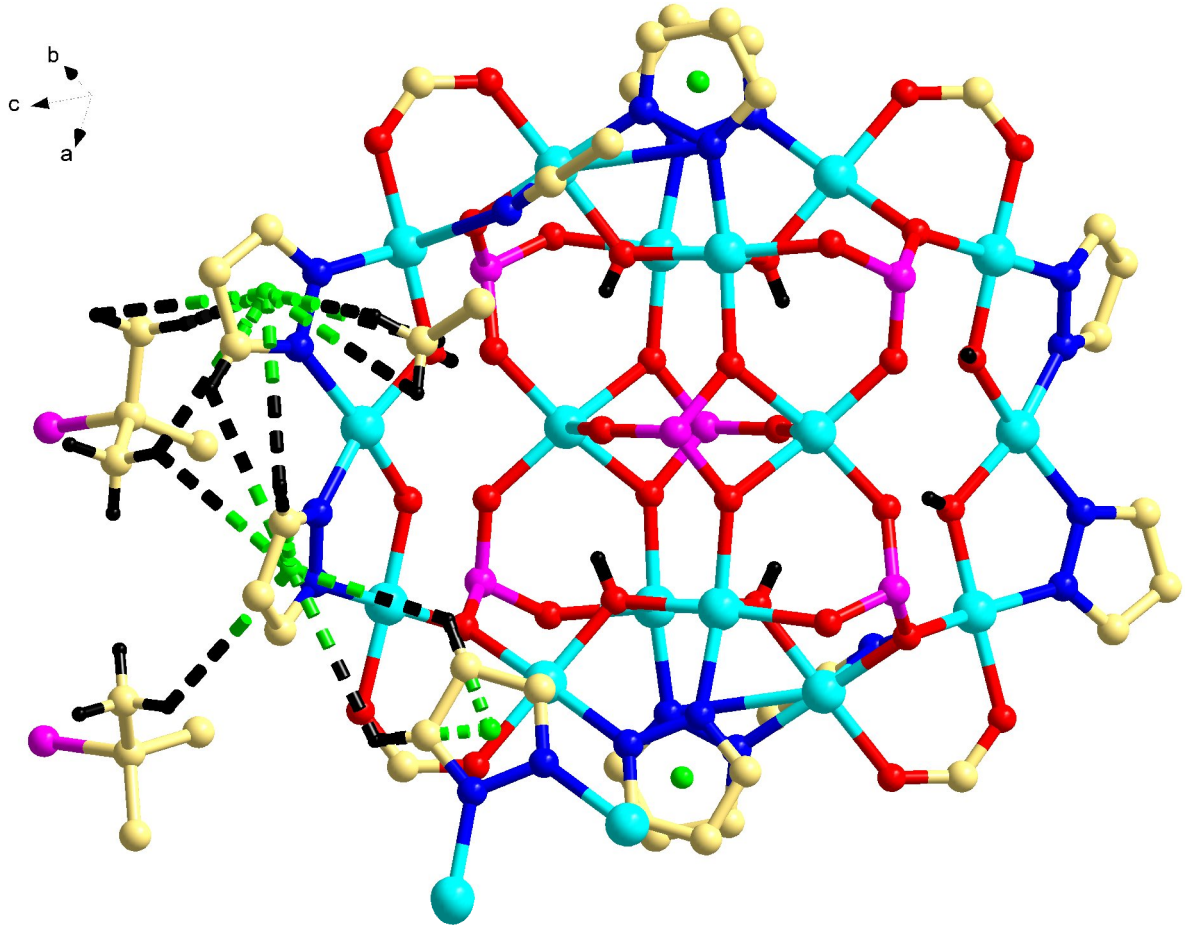
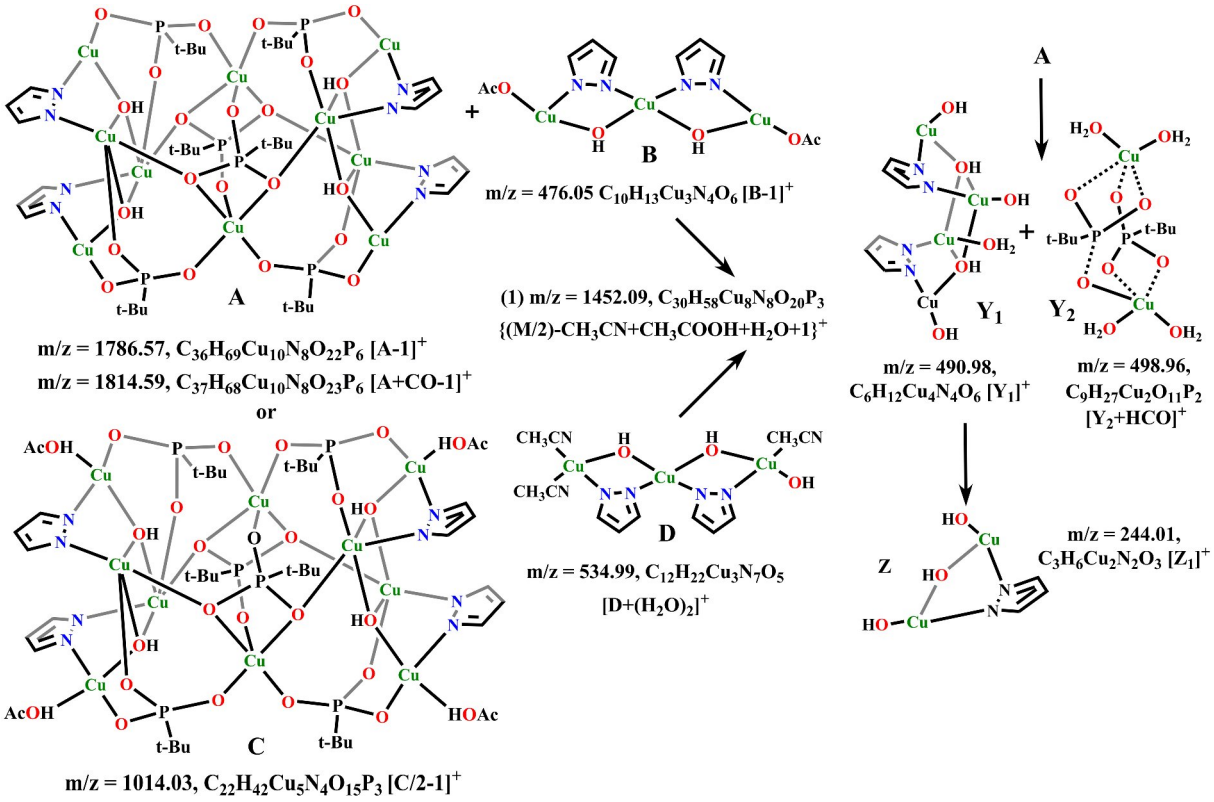


Figure S9. The structure of **1** showing the presence of various π···π and C-H··· π interactions. The bonding parameters are (a) for intramolecular interaction: $\pi_{pz}\cdots\pi_{pz}$ 3.808(6) Å; C5-H5$\cdots\pi_{pz}$ 3.538(2); C6-H6$\cdots\pi_{pz}$ 3.779(4); C16-H16$\cdots\pi_{pz}$ 2.954(5); C17-H17$\cdots\pi_{pz}$ 3.442(9) Å and (b) for intermolecular interactions C2S-H2S1$\cdots\pi_{pz}$ 2.824(6); C2S-H2S2$\cdots\pi_{pz}$ 3.302(8); C2S-H2S3$\cdots\pi_{pz}$ 3.897(6); C11-H11C$\cdots\pi_{pz}$ 3.556(6); C12-H12A$\cdots\pi_{pz}$ 2.948(3) Å.



Scheme S1. Plausible mechanism for the formation of **1** and various building blocks (**A**-**D** and **Y**-**Z**) that may be involved in the formation of cage **1**.

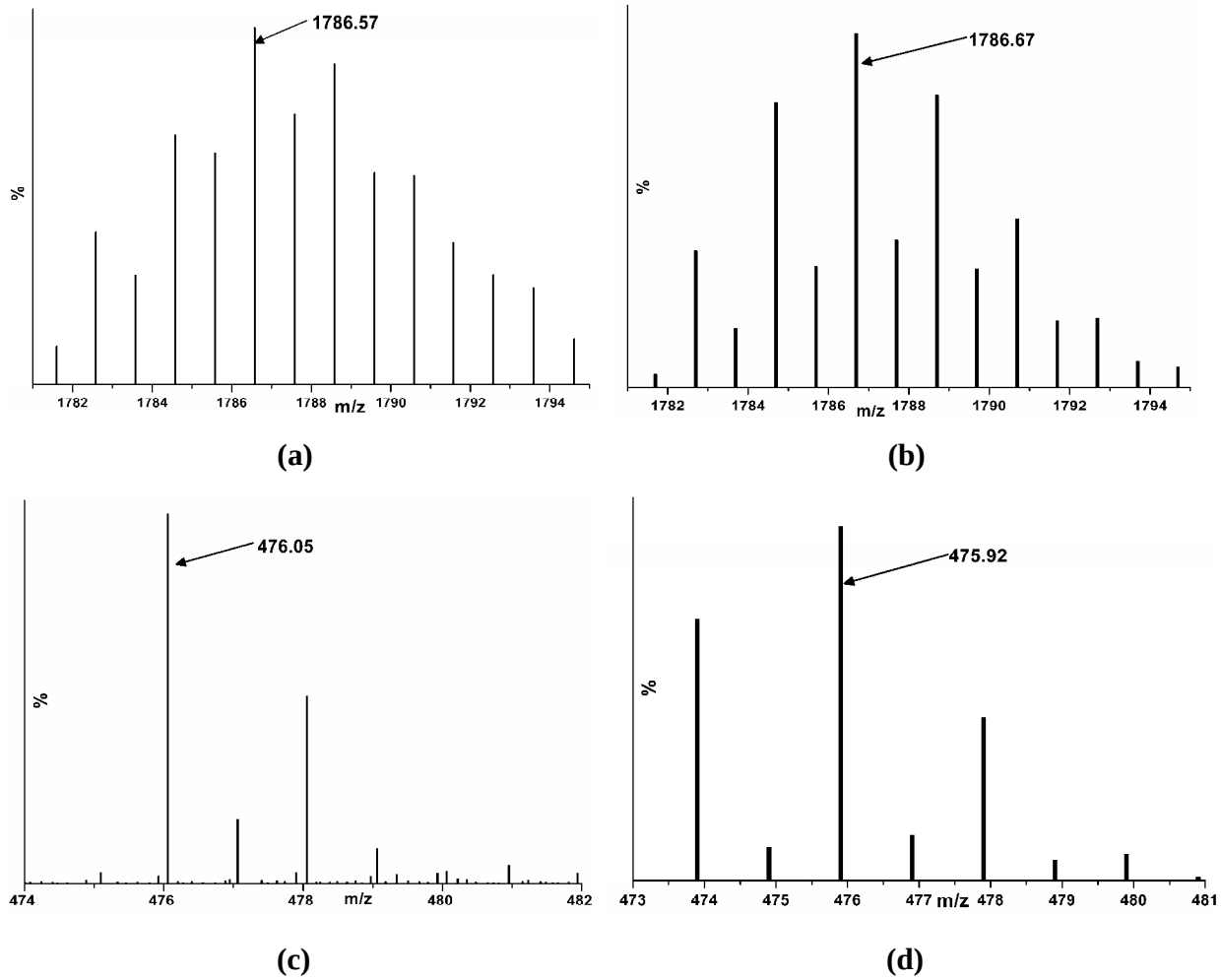


Figure S10. (a) and (b) Experimental and simulated ESI-MS spectra for the ions $C_{36}H_{69}Cu_{10}N_8O_{22}P_6$ $[A\text{-}1]^+$. (c) and (d) Experimental and simulated ESI-MS spectra for the ions $C_{10}H_{13}Cu_3N_4O_6$ $[B\text{-}1]^+$ (A and B are depicted in Scheme S1).

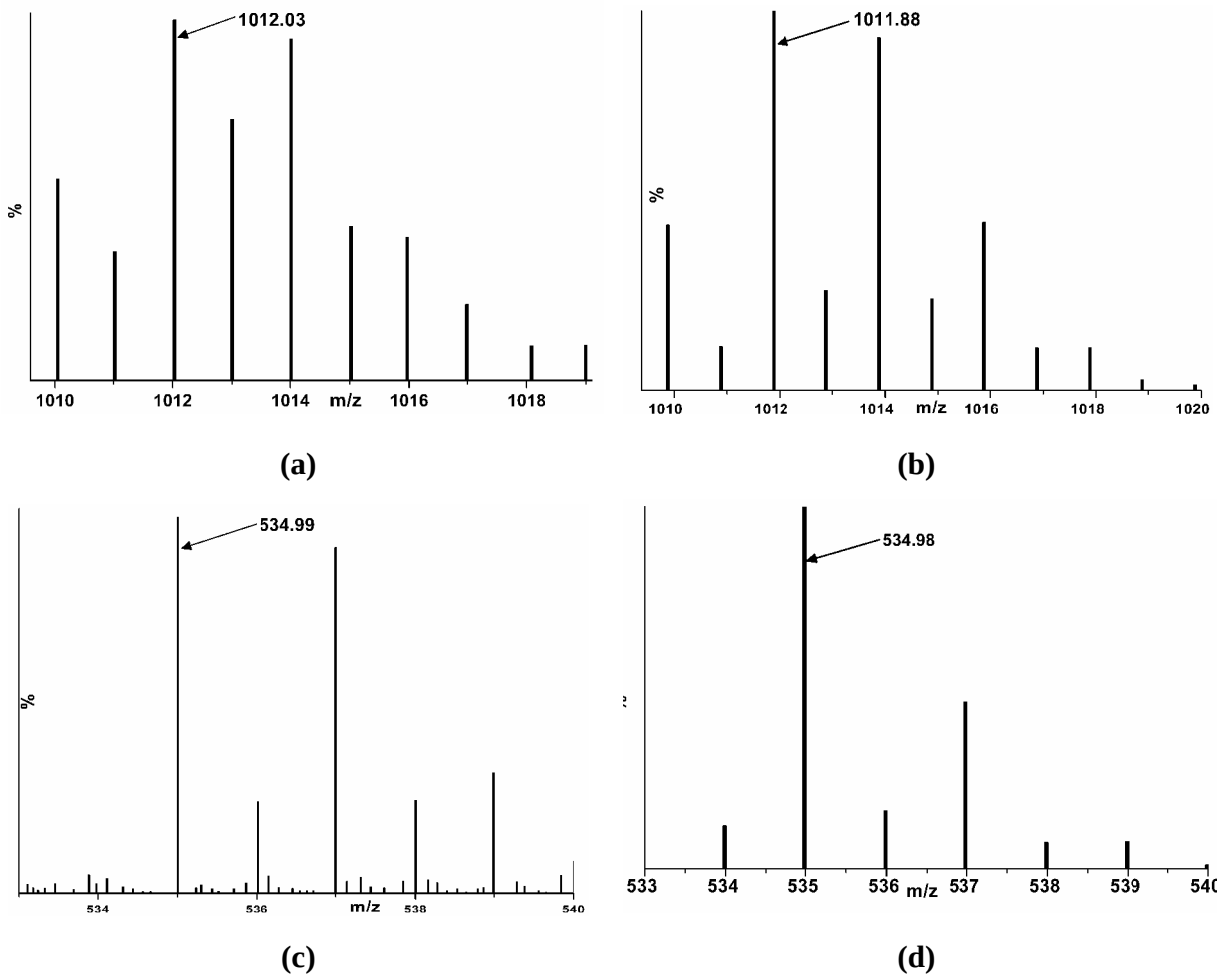


Figure S11. (a) and (b) Experimental and simulated ESI-MS spectra for the ions $C_{22}H_{42}Cu_5N_4O_{15}P_3$ $[C/2\text{-}1]^+$. (c) and (d) Experimental and simulated ESI-MS spectra for the ions $C_{12}H_{22}Cu_3N_7O_5$ $[D+(H_2O)_2]^+$ (C and D are depicted in Scheme S1).

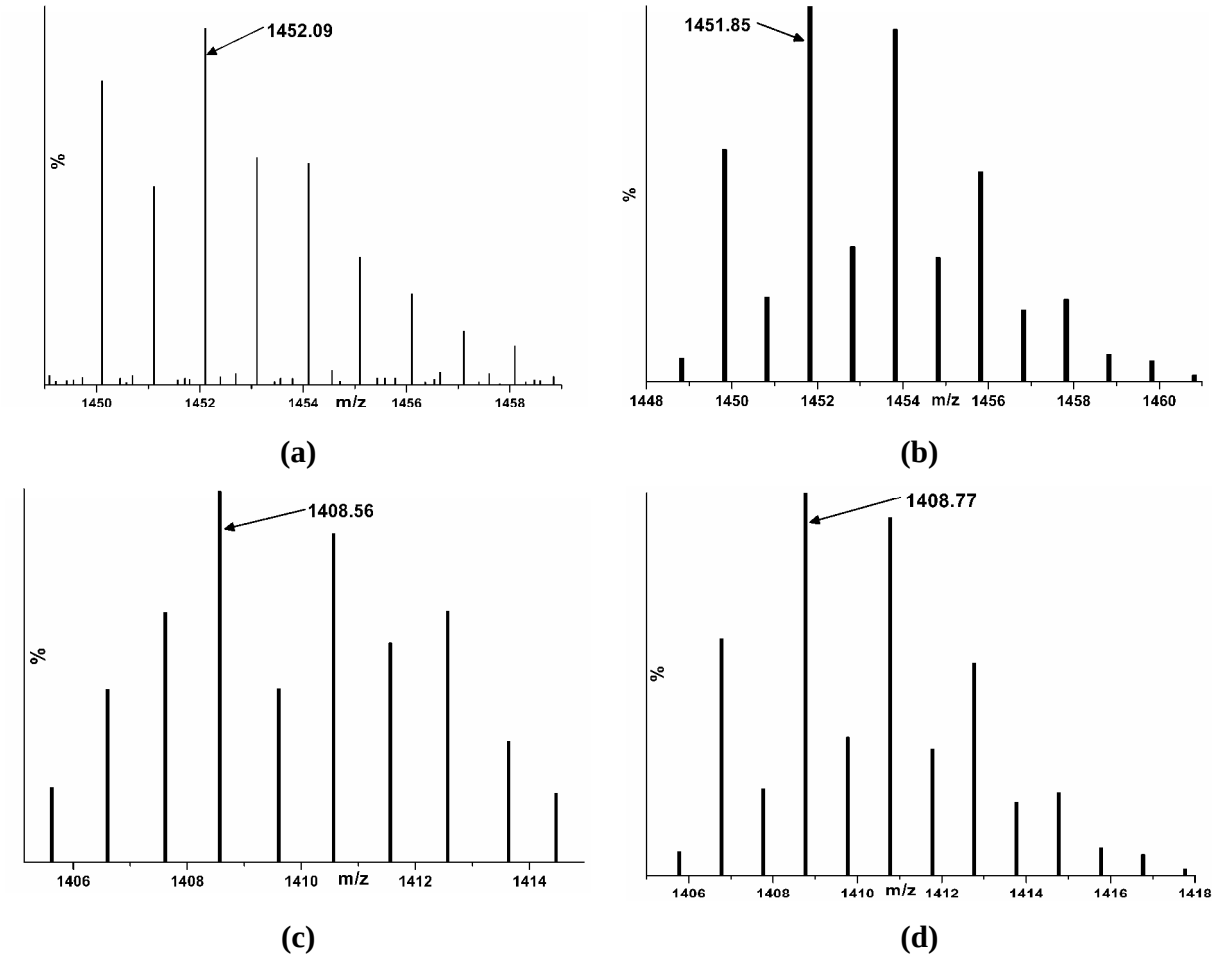


Figure S12. (a) and (b) Experimental and simulated ESI-MS spectra for the ions $C_{30}H_{58}Cu_8N_8O_{20}P_3$ $\{[M/2]\text{-}CH_3CN+CH_3COOH+H_3O\}^+$. (c) and (d) Experimental and simulated ESI-MS spectra for the ions $C_{30}H_{50}Cu_8N_9O_{17}P_3$ $[M/2\text{-}3]^-$.

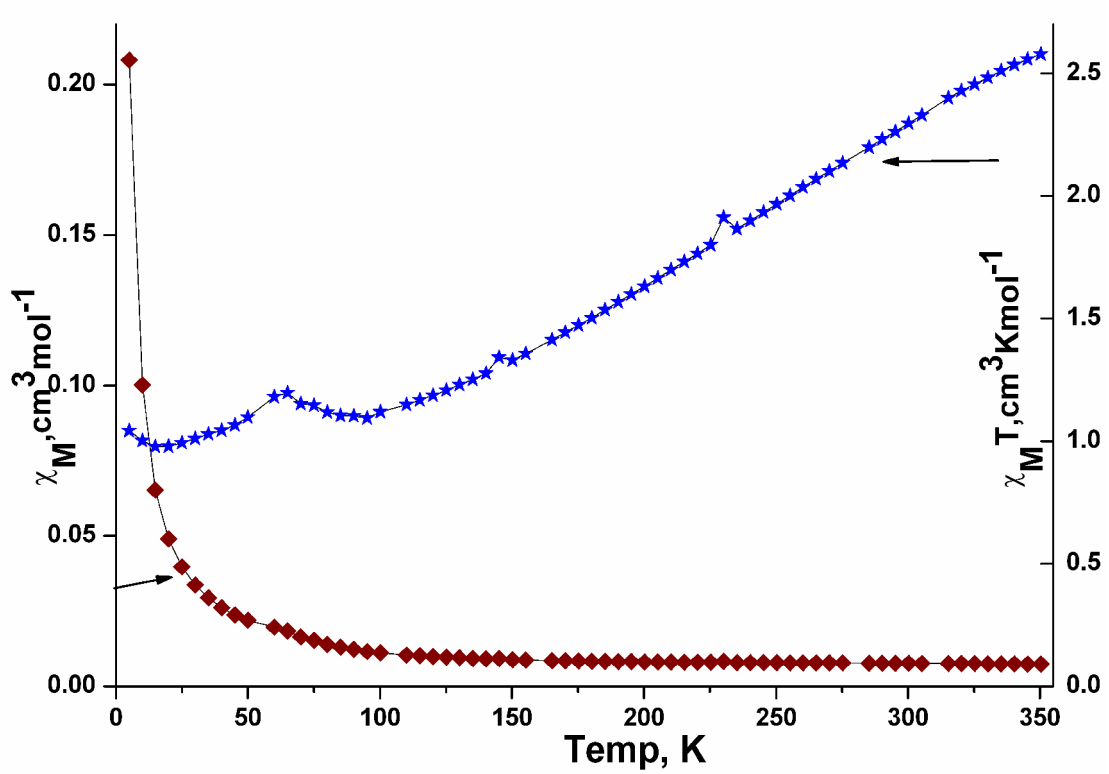


Figure S13. Temperature dependence of $\chi_m T$ at 10000 Oe of **1.**

Although, the precise reason for the magnetic ordering at around 65 K is not known, it may be either due to the formation of copper oxide or the phase change. Since the compound **1** has been formed due to *insitu* ethylacetate hydrolysis, it may be possible that it could lead to further hydrolysis and eventually forming a copper oxide. The complete delineation of these proposal is in progress

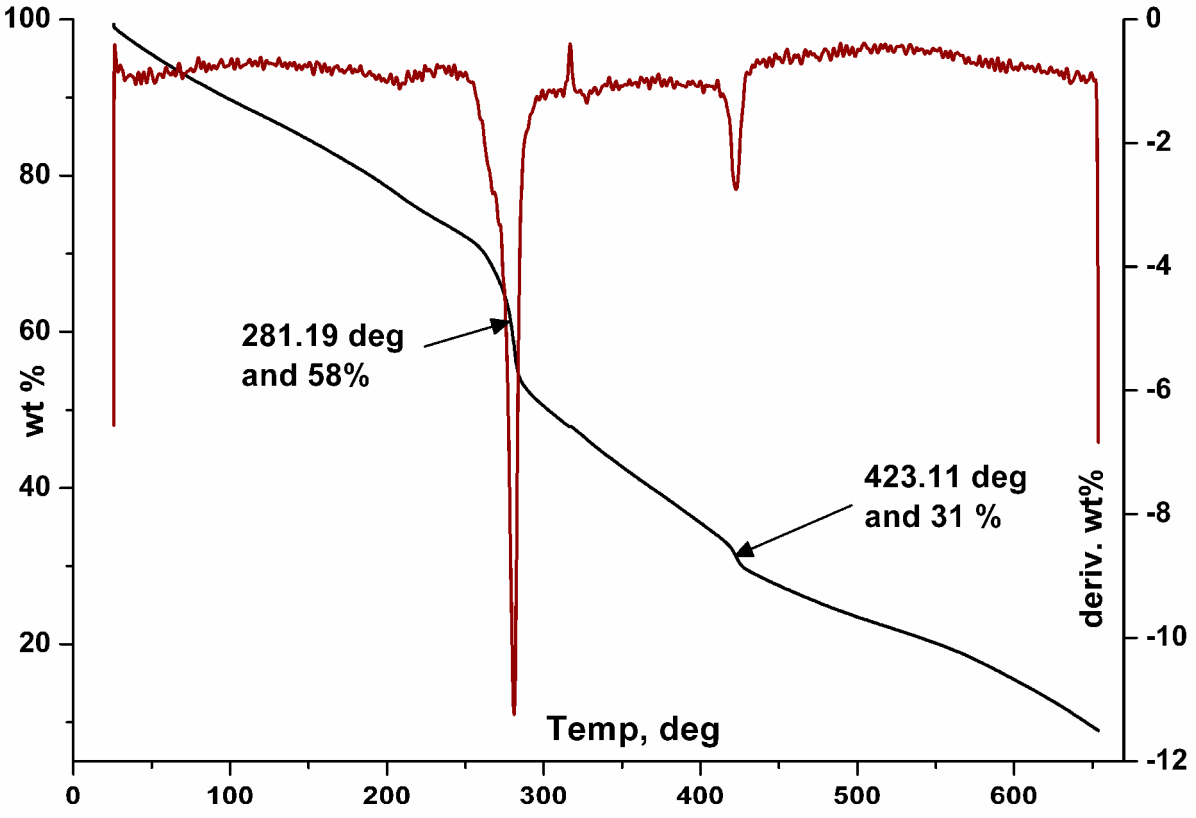
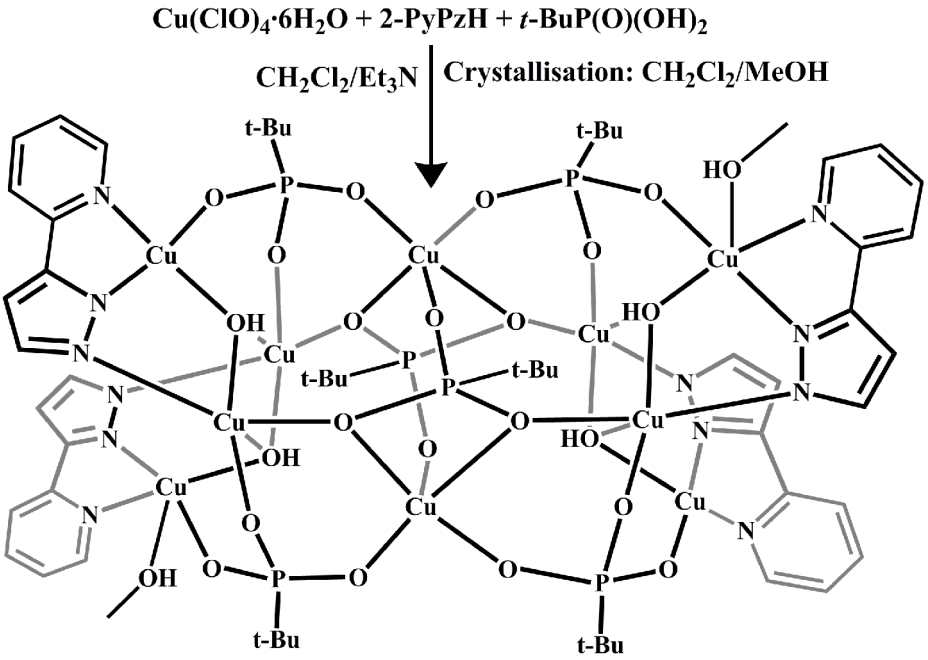
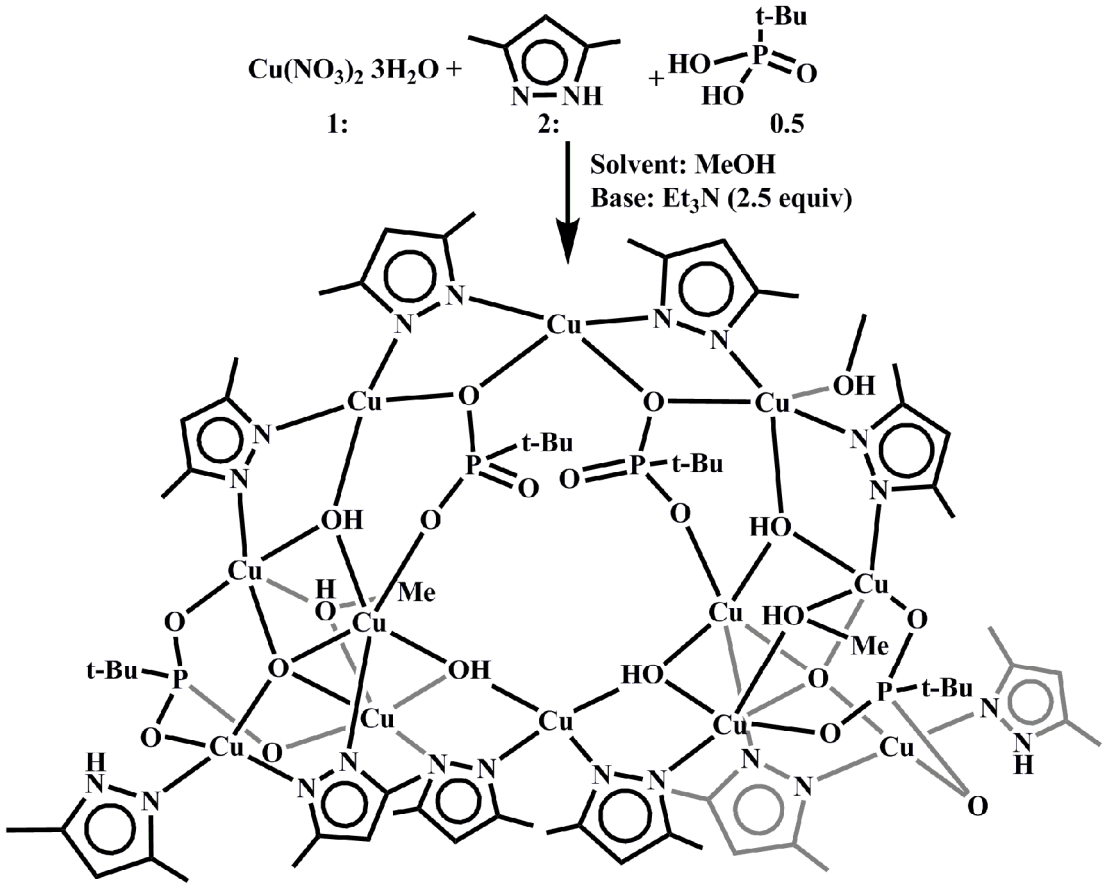


Figure S14. TGA trace of **1**. It shows an initial weight loss of 42% at around 281°C, which corresponds to the loss of **four acetate, two acetonitrile, two pyrazole and two [$Cu_3(OH)_2(Pz)_2$] molecules,** there is again a loss of about 17% at 423°C. About 10% (by weight) of residue remains until 650^{o}C.



Scheme S2. Synthesis of {[$Cu_5(\mu_3\text{-}OH)_2(t\text{-}BuPO_3)_3(2\text{-}PyPz)_2(MeOH)]_2\cdot(MeOH)_{10}\cdot(H_2O)_2$}.



Scheme S3. Synthesis of {[Cu_{12}(μ-DMPz)$_8$(η^1-DMPzH)$_2$(μ_4-O)$_2$(μ_3-OH)$_4$(μ_3-*t*-BuPO_3)$_4$]·(MeOH)$_3$}.

Table S1. Selected Bond lengths(Å) and angles (°) of **1.**[a]

Cu1-O1 1.956(4)	P2-O1* 1.569(4)	O5-Cu3-N5 87.0(2)	O16*-Cu8-O10* 86.77(16)
Cu1-O2 1.943(4)	P2-O11 1.512(5)	O5-Cu3-N4 162.7(2)	N1-Cu8-O15 164.3(2)
Cu1-O17 1.911(4)	P2-O12 1.519(6)	O4-Cu3-N4 85.4(2)	N1-Cu8-O10* 102.4(2)
Cu1-N2 1.929(5)	P3-O13 1.562(5)	O4-Cu3-N5 165.5(2)	O10*-Cu8-O15 93.21(17)
Cu2-O1 1.987(4)	P3-O14* 1.486(4)	N5-Cu3-N4 98.3(2)	Cu1-N2-N1 120.13(4)
Cu2-O3 1.945(5)	P3-O15 1.560(5)	O5-Cu4-N6 86.5(2)	Cu2-N3-N4 120.74(5)
Cu2-O4 1.871(5)	N1-C26 1.313(8)	O5-Cu4-O8 176.7(2)	Cu3-N5-N6 118.07(5)
Cu2-N3 1.951(6)	N1-N2 1.370(7)	O5-Cu4-O7 95.1(2)	Cu5-N7-N8 121.75(4)
Cu3-O4 1.886(5)	N2-C28 1.325(9)	O8-Cu4-O7 87.98(19)	O16-P1-O6 114.6(2)
Cu3-O5 1.887(5)	N3-C3 1.330(9)	N6-Cu4-O8 90.8(2)	O16-P1-O7 110.3(3)
Cu3-N4 1.955(6)	N3-N4 1.395(8)	N6-Cu4-O7 163.2(2)	O6-P1-O7 108.4(3)
Cu3-N5 1.966(5)	N4-C5 1.322(10)	O10-Cu5-N7 87.7(2)	O12-P2-O11 115.1(3)
Cu4-O5 1.884(5)	N5-C6 1.332(8)	O10-Cu5-O9 175.0(2)	O12-P2-O1* 108.3(3)
Cu4-O7 2.019(5)	N5-N6 1.374(8)	N7-Cu5-O9 91.6(2)	O11-P2-O1* 109.9(3)
Cu4-O8 1.948(5)	N6-C8 1.310(9)	O10-Cu5-O7 91.61(18)	O14-P3-O13 115.7(3)
Cu4-N6 1.969(6)	N7-C15 1.3338)	N7-Cu5-O7 173.1(2)	O14-P3-O15 114.8(3)
Cu5-O7 1.936(4)	N7-N8 1.374(7)	O9-Cu5-O7 89.63(19)	O13-P3-O15 99.1(3)
Cu5-O9 1.962(4)	N8-C17 1.338(9)	O10-Cu6-N8 87.0(2)	P1-O7-Cu4 129.0(3)
Cu5-O10 1.939(4)	N1S-C1S 1.131(11)	O10-Cu6-O13 92.06(18)	P1-O7-Cu5 120.01(3)
Cu5-N7 1.935(5)		O10-Cu6-O11 174.8(2)	P1-O6-Cu7* 134.48(3)
Cu6-O10 1.914(4)	N2-Cu1-O17 87.3(2)	N8-Cu6-O13 166.4(2)	P1-O16*-Cu8* 128.74(3)
Cu6-O11 1.930(4)	N2-Cu1-O1 170.1(2)	N8-Cu6-O11 90.1(2)	P2-O11-Cu6 126.40(3)
Cu6-O13 1.992(4)	N2-Cu1-O2 90.4(2)	O13 Cu6-O11 91.71(18)	P2-O12-Cu7 136.46(4)
Cu6-N8 1.954(5)	O17-Cu1-O1 93.83(19)	O6*-Cu7-O12 89.11(19)	P2*-O1-Cu1 120.71(3)
Cu7-O6* 1.891(4)	O17-Cu1-O2 174.5(2)	O6*-Cu7-O13 169.50(19)	P2*-O1-Cu2 127.82(3)
Cu7-O12 1.892(4)	O1-Cu1-O2 89.34(19)	O6*-Cu7-O15 98.19(18)	P3-O13-Cu6 137.15(3)
Cu7-O13 2.008(4)	O4-Cu2-O3 177.0(2)	O6*-Cu7-O14 90.60(18)	P3-O15-Cu8 137.74(3)
Cu7-O14 2.293(5)	O4-Cu2-O1 94.4(2)	O12-Cu7-O13 98.05(18)	P3-O15-Cu7 94.23(2)
Cu7-O15 2.003(5)	O4-Cu2-N3 85.3(2)	O12-Cu7-O15 162.8(2)	P3-O13-Cu7 93.78(3)
Cu8-O10* 2.420(5)	O3-Cu2-N3 91.7(2)	O12-Cu7-O14 101.58(19)	P3*-O14-Cu7 135.9(3)
Cu8-O15 1.969(4)	O3-Cu2-O1 88.62(2)	O13-Cu7-O15 72.87(17)	Cu1-O1-Cu2 103.82(2)
Cu8-O16* 1.968(5)	N3-Cu2-O1 176.4(2)	O13-Cu7-O14* 94.02(2)	Cu2-O4-Cu3 124.63(3)
Cu8-O17 1.934(4)	O5-Cu3-O4 93.5(2)	O15-Cu7-O14 93.88(2)	Cu3-O5-Cu4 127.0(4)
Cu8-N1 1.944(5)		O17-Cu8-O16* 174.89(19)	Cu4-O7-Cu5 106.43(2)
		O17-Cu8-N1 86.8(2)	Cu5-O10-Cu6 123.07(2)
P1-O6 1.510(5)		O17-Cu8-O15 91.80(19)	Cu6-O13-Cu7 128.01(3)
P1-O7 1.563(5)		O17-Cu8-O10* 89.06(17)	Cu7-O15-Cu8 127.83(2)
P1-O16 1.517(5)		O16*-Cu8-N1 91.24(19)	Cu8-O17-Cu1 122.74(2)
		O16*-Cu8-O15 91.38(18)	

[a]For labeling scheme see Figure S6. * indicates the symmetrically related atoms and the symmetry operators are 1-x, 2-y, 1-z.

Table S2. Summary of the coordination environment, geometry around copper atoms, τ_5 and τ_4 values in **1**.				
Cu (II) Centers	**CN**[a]	**Coordination Environment**	**Position**	**Geometry**[b]
Cu1, Cu2 and Cu1*, Cu2*	4	1N, 3O (1N: 1 pz 3O: 1 O-P, 1 O-C, 1 μ_3-OH)	*wing and crown*	square pyramidal
Cu3 and Cu3*	4	2N and 2O (2N: 2 pz 2O: 2 μ-OH)	*crown*	square planar
Cu4, Cu5 and Cu4*, Cu5*	5	2N and 3O (1N: 1 pz, 1 CH_3CN 3O: 1 O-P, 1 O-C, 1 μ_3-OH)	*wing and crown*	square planar
Cu6, Cu8, Cu6*and Cu8*	5	1N and 4O (N: pz; 4O: 2 μ_3-OH, 2 O-P)	*wing*	square pyramidal
Cu7 and Cu7*	5	5O (5 O-P)	*rim*	square pyramidal
[a]Coordination Number. [b]Slight distortion from ideal geometry is seen.				
Trigonality Index values (τ_5)[1]: Cu4 0.028; Cu5 0.217; Cu6 0.176; Cu7 0.114; Cu8 0.135.				
Four coordinate geometry Index values (τ_4)[2]: Cu1 0.043; Cu2 0.126; Cu3 0.224.				

1) Trigonality index or five coordinate geometry index value (τ_5): Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc. Dalton Trans.* **1984**, 1349. $\tau_5 = (\beta-\alpha)/60°$. Where, β is the greater of the basal angles. For square pyramidal geometry $\tau_5 = 0$ (since $\alpha=\beta=180°$); trigonal bipyramidal geometry $\tau_5 = 1$ (since α and $\beta \neq 180°$).
2) Four coordinate geometry index value (τ_4): Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955. $\tau_4 = [360°-(\alpha+\beta)]/141°$. α and β are the two largest bond angles of the four coordinate metal complexes. $\tau_4 = 0$ for perfect square planar geometry (since 360-2(180) = 0) and $\tau_4 = 1$ for tetrahedral geometry (since 360-2(109.5) = 141).

Table S3. Summary of the number of rings present in cage **1.**		
Ring system	**No**	**Atoms involved in the ring formation**
26-membered ring	1	Cu1, O2, C1, O3, Cu2, N3, N4, Cu3, N5, N6, Cu4, O8, C13, O9, Cu5, N7, N8, Cu6, O11, P2, O12, Cu7, O15, Cu8, N1 and N2
	2	Symmetry related atoms as in above
16-membered ring	1	Cu1, O1, Cu2, O4, Cu3, O5, Cu4, O7, Cu5, O10, Cu6, O13, P3, O15, Cu8 and O17
	2	Symmetry related atoms as in above
12-membered ring	1	Cu6, O13, P3, O15, Cu8, O16, P1*, O6*, Cu7, O12, P2 and O11
	2	Symmetry related atoms as in above
	3	Cu4, O5, Cu3, O4, Cu2, O1, P2*, O12*, Cu7*, O6, P1 and O7
	4	Symmetry related atoms as in above
	5	Cu5*, O7*, P1*, O16, Cu8, O17, Cu1, O1, P2*, O11*, Cu6* and O10*
	6	Symmetry related atoms as in above
10-membered ring	1	Cu8, O15, P3, O14, Cu7*, O12*, P2*, O1*, Cu1 and O17
	2	Symmetry related atoms as in above
	3	Cu7*, O14, P3, O13, Cu6, O10, Cu5, O7, P1 and O6
	4	Symmetry related atoms as in above
8-membered ring	1	Cu1, O1, P2*, O11*, Cu6*, O13*, Cu7* and O12*
	2	Symmetry related atoms as in above
	3	Cu5, O7, P1, O16*, Cu8*, O15*, Cu7* and O6
	4	Symmetry related atoms as in above
6-membered ring	1	Cu7, O6*, P1*, O16, Cu8 and O15
	2	Symmetry related atoms as in above
	3	Cu8, O16, P1*, O7*, Cu5* and O10*
	4	Symmetry related atoms as in above
	5	Cu6, O13, Cu7, O12, P2 and O11
	6	Symmetry related atoms as in above
	7	Cu6, O11, P2, O1*, Cu1* and O17*
	8	Symmetry related atoms as in above
	9	Cu5, O7, Cu4, O8, C13 and O9

	10	Symmetry related atoms as in above
	11	Cu2, O3, C1, O2, Cu1 and O1
	12	Symmetry related atoms as in above
	13	Cu2, N1S, Cu1, O2, C1, O3
	14	Symmetry related atoms as in above
5-membered ring	1	Cu4, O5, Cu3, N5 and N6
	2	Symmetry related atoms as in above
	3	Cu3, O4, Cu2, N3 and N4
	4	Symmetry related atoms as in above
	5	Cu1, N1, N2, Cu8 and O17
	6	Symmetry related atoms as in above
	7	Cu5, N7, N8, Cu6 and O10
	8	Symmetry related atoms as in above
4-membered ring	1	Cu7, O13, P3 and O15
	2	Symmetry related atoms as in above
	3	Cu8, O17, Cu6* and O10*
	4	Symmetry related atoms as in above
	5	Cu4, O7, Cu5 and N1S
	6	Symmetry related atoms as in above