### **Electronic Supplementary Information for**

# First hexanuclear copper(II) pyrophosphate through hydrolysis of phosphodiester with a dicopper complex

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### **Experimental Procedures:**

#### Materials:

All reagents were purchased from commercial sources and of reagent quality. Air sensitive and moisture sensitive compounds were prepared and handled using standard Schlenk techniques. Solvents were purified by standard procedures.<sup>[1]</sup> Ethanol was purchased from Hayman (England) and used as received.

**Physical Measurements**. C, H, N analysis was performed on Perkin-Elmer 2400 Series CHNS/O Analyser. Electronic absorption spectra were recorded on CARY 5E model and IR spectra as KBr disk on Shimadzu IR–470 spectrophotometer. NMR spectra were recorded either on a BRUKER AVANCE-400 or JEOL GMX-400 spectrometer. <sup>31</sup>P NMR spectra were recorded at 300 K using 10% D<sub>2</sub>O<sub>aq</sub> solution with 85% H<sub>3</sub>PO<sub>4</sub> acid as an internal standard. The magnetic moment of complexes was calculated by Evans method using appropriate deuteriated solvent.<sup>[2]</sup> X-band EPR spectra were performed on Varian E-112 spectrometer at 77 K. Mass spectra were obtained in acetonitrile/water mixture on a Q-Tof-Mass Spectrometer equipped with a standard electrospray source. The TGA analysis of **2** was done using sample (2.39 mg) loaded in aluminum crucible on Perkin Elmer TGA Model 7 under nitrogen atmosphere (20 cc/min) with linear heating of 20 °C/min. pH measurements were done on DIGITAL pH meter of MODEL 2001 from DIGISUN ELECTRONICS SYSTEMS attached with combined glass electrode.

## (i) Synthesis.

The ligand, **L** was synthesized by our group.<sup>[3]</sup>

*Caution*. Perchlorate salts of organic compounds are potentially explosive; these compounds must be prepared and handled with great care!

**[LCu(OH)]**<sub>2</sub>(**ClO**<sub>4</sub>)<sub>2</sub>, **1**. To a stirred solution of copper(II) perchlorate hexahydrate (0.31 g, 0.84 mmol) in EtOH (3 mL) was added the ethanolic solution (4 mL) of **L** (0.25 g, 0.86 mmol) and the resulted clear green solution was stirred for 5 min. To this triethyl amine (120 uL, 0.86 mmol) was added and a lavender precipitate formed instantly. This was stirred for 30 min and the reaction mixture was filtered and the complex was dried in vacuum to give 0.36 g (92 %) of **1**. Single crystals were obtained by slow evaporation of CH<sub>3</sub>CN solution of the complex, **1**. Anal. Calcd for C<sub>40</sub>H<sub>36</sub>Cl<sub>2</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>8</sub>: C, 51.50; H, 4.10; N, 6.00. Found: C, 51.59; H, 4.31; N, 6.45 %. UV-Vis [CH<sub>3</sub>CN,  $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)]: 615 (120). IR (mull, cm<sup>-1</sup>): 3600 (s), v(OH<sup>-</sup>); 1092 (bs), v(ClO<sub>4</sub><sup>-</sup>);  $\mu$  (CD<sub>3</sub>CN): 1.47 BM/Cu(II). ESI-MS (CH<sub>3</sub>CN/H<sub>2</sub>O): m/z 832 (13 %), [M-ClO<sub>4</sub><sup>-</sup>)]<sup>+</sup>; m/z 408 (16 %), [LCu(OH<sup>-</sup>)(CH<sub>3</sub>CN)]<sup>+</sup>; m/2z 347 (39 %), [L<sub>2</sub>Cu(OH<sub>2</sub>)(CH<sub>3</sub>CN)]<sup>2+</sup>; 287 (7 %), [(L+H)]<sup>+</sup>.

## $[L_6Cu_6(CH_3CN)_2(H_2O)_4(P_2O_7)_2](ClO_4)_4$ . 2CH<sub>3</sub>CN. 2H<sub>2</sub>O, 2.

**Method A:** To a stirred solution of complex **1** (0.123 g, 0.13 mmol) in acetonitrile (8 mL), added dropwise aqueous solution of the NaBNPP (0.048 g, 0.13 mmol). The resulting bluish green solution was refluxed at 50°C for 7 hrs. The dark green supernate with little bluish green mass was obtained. This was filtered and the green mass (0.024 g) was discarded. The filtrate afforded bluish green shiny material after removal of acetonitrile. X-ray quality crystals (0.069 g, 71%, based on P) were obtained by vapor diffusion of diethyl ether into the acetonitrile solution of the complex. Anal. Calcd for  $C_{124}H_{122}Cl_4P_4N_{14}O_{34}Cu_6$ : C, 49.72; H, 4.07; N, 6.55.

Found: C, 50.99; H, 3.73; N, 6.78. UV-Vis [CH<sub>3</sub>NO<sub>2</sub>,  $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)]: 374 (1182), 691 (362). IR (mull, cm<sup>-1</sup>): 3457 (bs) v(OH<sub>2</sub>); 2255 (s) v(CH<sub>3</sub>CN); 1255 (bs) v(PO<sub>2</sub><sup>-</sup>, as); 1071 (bs) v(PO<sub>2</sub><sup>-</sup>, sy); 1101 (bs) v(ClO<sub>4</sub><sup>-</sup>). Magnetic moment (Evans, CD<sub>3</sub>NO<sub>2</sub>): 1.81 BM/Cu(II). EPR (77 K, CH<sub>3</sub>CN): g<sub>II</sub> = 2.26, g<sub>⊥</sub> = 2.04, A<sub>II</sub> = 160 G. ESI-MS (CH<sub>3</sub>CN): m/z 875 (23 %) [L<sub>2</sub>Cu<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)]; m/2z 347 (34 %), [L<sub>2</sub>Cu(OH<sub>2</sub>)(CH<sub>3</sub>CN)]<sup>2+</sup>; m/z 287 (100 %), [L+H]<sup>+</sup>.

**Method B.** To a stirred solution of  $Cu(ClO_4)_2.6H_2O$  (0.14 g, 0.37 mmol) in acetonitrile (4 mL), added acetonitrile solution (6 mL) of the ligand **L** (0.11 g, 0.37 mmol) to give intense green clear solution. To this, aqueous solution (1.5 mL) of tetrasodium pyrophosphate (0.035 g, 0.14 mmol) was added. Immediately, blue precipitate with green supernate was observed. After 2 h of stirring, the reaction solution was filtered to give blue precipitate with green filtrate. The blue complex was dried in vacuo to obtain 58% (0.11 g) of complex **2**. The formation of **2**, by this method is confirmed by comparing with the spectral data of the hydrolytic product, **2** from method A.

[L<sub>2</sub>Cu<sub>2</sub>(OH)(DPP)](ClO<sub>4</sub>)<sub>2</sub>. 2CH<sub>3</sub>CN. H<sub>2</sub>O, **3**. To a stirred solution of complex **1** (0.064 g, 0.068 mmol) in acetonitrile (5 mL), was added, drop-wise a solution of the diphenyl phosphate (0.48 mL, 0.144 M) in the same solvent. The resulting green clear solution was stirred for 2 h and removal of solvent yielded greenish blue solid which was dried in *vacuo* to obtain 0.053 g (68%) of complex **3**. X-ray quality crystals were obtained by vapour diffusion of diethyl ether in to an acetonitrile solution of complex **3** to obtain **3**. **2CH<sub>3</sub>CN**. **H**<sub>2</sub>**O**. Anal. Calcd for C<sub>52</sub>H<sub>47</sub>N<sub>4</sub>Cl<sub>2</sub>Cu<sub>2</sub>O<sub>13</sub>P: C, 53.69; H, 3.98; N, 4.82. Found: C, 53.72; H, 4.05; N, 4.94%. UV-Vis [CH<sub>3</sub>CN,  $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)]: 698 (174). IR (KBr disc, cm<sup>-1</sup>): 3479 v(OH<sub>2</sub> and OH); 1202 v(PO<sub>2</sub>); 1093 v(ClO<sub>4</sub>). ESI-MS (CH<sub>3</sub>CN): *m/z*, 1065 (8%), [M-ClO<sub>4</sub><sup>-</sup>)]<sup>+</sup>; *m/2z*, 598 (30%), [LCu(DPP)]<sub>2</sub><sup>2+</sup>; *m/2z*, 408 (20%), [LCu(OH)(CH<sub>3</sub>CN)]<sub>2</sub><sup>2+</sup>; 285 (33%), [L-2H)]<sup>+</sup>.

X-Ray crystallographic data collection and structure refinement. Single crystal X-ray data collection of 1 and 3 were collected on a Bruker Smart Apex CCD diffractometer equipped with graphite-monochromated Mo-K<sub>a</sub> radiation ( $\lambda = 0.71073$ Å) at 273 and 223 K, respectively. The data collection of 2 was carried out on a Enraf-Nonius CAD-4 diffractometer equipped with Cu-K<sub> $\alpha$ </sub> ( $\lambda$  = 1.541 Å) radiation. The reflections were corrected for Lorentz and polarization effects and empirical absorption corrections were applied using the SADABS program. The space groups were determined from systematic absences and confirmed by the results of refinement. The structures were solved by direct methods using the SHELXL software suit (SHELXS 86),<sup>[4]</sup> and refined by full-matrix least squares method (on F2; SHELXL 97).<sup>[5]</sup> All non-H (except some of the solvent molecules) were refined with anisotropic displacement parameters and all H atoms of the organic ligands were placed at idealized positions and refined as riding atoms. A total of 56 restraints were used during refinement of 2. The restraints were used on distances related to the anions (ClO<sub>4</sub>), acetonitrile and water molecules. These restraints were applied to maintain chemically meaningful geometry to these moieties. Both anions in asymmetric unit are disordered and the refinement is carried out with sum of the disordered fragments constrained as 1. The oxygen atoms of the perchlorate anions were assigned only isotropic displacement parameters (anisotropic refinement is leading to bad standard deviations for thermal parameters). The crystallographic data of 1, 2, and 3 were listed in Table S1. Selected bond lengths and bond angles of 2 are given in Table S2. The 1D layer structure of 2 with C..H. $\pi$  interactions is shown in Figures S1.



**Figure S1:** The 1D-layer arrangement of hexamer, 2 showing C-H  $\pi$  interactions

(ii) Kinetics of BNPP Hydrolysis. The rate of hydrolysis of BNPP by complex 1 was carried out by spectrophotometric method with varying solution concentrations of [1] = 0.5-2.5 mM at constant [NaBNPP] = 12 mM. In a typical reaction, acetonitrile dicopper (bis-mu)hydroxo solution mL) complex, (6 of [LCu(OH)]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>. 1 plus an aqueous solution of NaBNPP (0.4 mL) with final concentrations as mentioned above was heated at 50  $^{\circ}$ C. After every 1 h, 50  $\mu$ L of the reaction solution was withdrawn and diluted to 1.1 mL Tris-HClO<sub>4</sub> buffer (pH 8.3, 0.05 M) in 0.5 cm UV-cuvette assembly followed by measurement of the increase in absorbance at 400 nm. The rate of the reaction was calculated from the plot of [pNP] vs time (Figure S2, a) and the pseudo-first order rate constant  $k_{obs} = (1.49 \pm 0.05) \times 10^{-10}$  $^{5}$  s<sup>-1</sup> was calculated from the plot of rate vs [1] (Figure S2, b). All the kinetic data were analyzed using Microsoft Origin.



**Figure S2.** (a) Plot of [pNP] vs time (b) rate vs [1] in CH<sub>3</sub>CN;  ${}^{[1]/mM}$  [1] = 0.5 – 2.5 mM; [NaBNPP] = 12 mM

(iii) Binding Studies. Binding of DPP<sup>-</sup> to the dicopper (bis-mu)hydroxo complex,  $[LCu(OH)]_2(ClO_4)_2$ , **1** was studied by electronic absorption spectroscopy. To the acetonitrile solution of  $[LCu(OH)]_2(ClO_4)_2$  (3.17 mM, 2.27 mL) was added aliquots of DPP through micro-litre syringe (5  $\mu$ L, 0.144 M, 0.1 equivalent). After each addition, the solution was stirred for 1 min and the visible spectrum was recorded (Figure S3, a). The binding constant, K was calculated from the plot of 1/[DPP] against Ao/(Ao-A) which yields a straight line with the intercept equal to negative of the binding constant.<sup>[6]</sup> A<sub>0</sub> and A denote the absorbance at a particular wavelength (697 nm) in absence and in presence of DPP, respectively. [DPP] is the concentration of the diphenyl phosphate solution added to the [LCu(OH)]\_2(ClO\_4)\_2, **1** in CH<sub>3</sub>CN. The binding constant was calculated to be 250 ±17 M<sup>-1</sup> (Figure S3, b).



**Figure S3.** (a) Electronic spectral changes for the stepwise addition of DPP (5-60 uL, 0.144 M) to  $[LCu(OH)]_2(ClO_4)_2$ , **1** (3.17 mM) in CH<sub>3</sub>CN; (b) the binding constant plot for the same.



**Figure S4.** The <sup>31</sup>P NMR spectrum in 10% D<sub>2</sub>O (pH = 8) showing the cleavage of BNPP into Pi, NPP and PPi (PPi: NPP: Pi 11: 36: 53%). Hydrolysis conditions: [BNPP] = 10.3 mM, [1] = 10.3 mM, T = 50 °C, t = 36 h. The <sup>31</sup>P NMR spectrum shows no unreacted BNPP ( $\delta$  -11 ppm).



Figure S5. The TGA-DTA plot of 2 under N<sub>2</sub> atm



**Figure S6.** X-Band (9.10 GHz) EPR spectrum of **2** in CH<sub>3</sub>CN/water at 77 K, scan range = 2200 - 4200 G, microwave frequency = 9.10 GHz, modulation amplitude = 40 G, modulation frequency = 100 KHz, microwave power = 10 mW.

parameter	1	2.2CH <sub>3</sub> CN.2H <sub>2</sub> O	3.2CH <sub>3</sub> CN.H <sub>2</sub> O
Diffractometer	CCD-Bruker	CAD4	CCD-Bruker
	Kappa Apex2		Kappa Apex2
X-ray source	$Mo(K_{\alpha})$	$Cu(K_{\alpha})$	$Mo(K_{\alpha})$
λ, Å	0.71073	1.541	0.71073
CCDC number	615837	615835	615836
MF	$C_{40}H_{38}Cl_2Cu_2N_4O_{10}\\$	$C_{128}H_{132}Cl_4Cu_6N_{16}O_{36}P$	$C_{56}H_{55}Cl_{2}Cu_{2}N_{6}O_{14}P$
Fwt	932.72	3117.42	1265.01
Temp, K	293(2)	293(2)	100(2)
Crystal system	monoclinic	triclinic	monoclinic
Space group	P2(1)/c	Pī	P2(1)/n
a, Å	20.2323(8)	15.990(4)	14.4129(3)
b, Å	9.1681(4)	16.422(2)	26.9168(5)
c, Å	20.8139(8)	16.724(4)	14.6457(3)
α, deg	90	105.052(12)	90
β, deg	95.760(2)	103.96(2)	98.074(1)
γ, deg	90	116.852(18)	90
V, Å <sup>3</sup>	3841.3(3)	3440.4(12)	5625.47(19)
Z	4	1	4
F(000)	1912	1602	2608
$D_c mg/m^3$	1.613	1.505	1.494
Reflections	85833	13014	64588
measured Reflections used	$6051[I > 2\sigma(I)]$	9514 [I>2σ(I)]	8432 [I>2σ(I)]
Abs. coeffi. mm <sup>-1</sup>	1.312	2.866	0.951
No of refined	531	903	767
parameters			
GOF	1.171	1.055	1.147
R <sup>a</sup>	0.0369	0.0500	0.0447
Rw <sup>b</sup>	0.0932	0.1519	0.1201

## Table S1.Crystallographic data for 1-3

<sup>a</sup>R = 
$$\sum ||F_o| - |F_c|| / \sum |F_o|, {}^{b}R_w = [\sum w(|F_o|^2 - |F_c|^2) / \sum w(F_o^2)^2]^{1/2}$$
  
w =  $1/[(\sigma(F_o^2))^2 + (0.0429P)^2 + 9.3125P]$  (1)  
 $1/[(\sigma(F_o^2))^2 + (0.0929P)^2 + 3.7550P]$  (2)  
 $1/[(\sigma(F_o^2))^2 + (0.0727P)^2 + 7.3165P]$  (3)

Cu-Cu Bond Parameters (Å)					
Distances (Å)					
Cu1-Cu2	4.343	Cu3-Cu3'	7.396		
Cu1-Cu3	6.160	Cu1-Cu2'	7.267		
Cu2 -Cu3	4.988	Cu1- Cu3'	6.016		
Cu1- Cu1'	9.673	Cu2- Cu3'	5.234		
Cu2- Cu2'	7.061	Cu3- Cu2'	5.234		
Cu-N Bond Parameters					
Distances (Å)		Angles (deg)	)		
Cu1-N1	2.070(3)	NI- Cu 1-N2	81.73(14)		
Cu1-N2	2.010(3)	N2- Cu 1-N7	92.61(16)		
Cu2-N3	2.061(3)	N1- Cu1-N7	93.06(16)		
Cu2-N4	1.989(3)	N3- Cu2-N4	82.01(14)		
Cu3-N5	2.076(3)	N6- Cu 3-N5	81.87(13)		
Cu3-N6	1.995(3)				
Cu-O Bond Parameters					
Distances (Å)		Angles (deg)			
Cu1-O1	1.934(3)	O1-Cu1-O7	95.75(11)		
Cu2-O3	1.920(3)	O3-Cu2-O5	97.17(11)		
Cu3-O6	1.916(2)	O3-Cu2-O8	90.36(15)		
Cu2-O8	2.391(4)	O5-Cu2-O8	89.96(13)		
Cu2-O5	1.939(3)	O6-Cu3-O2'	97.23(11)		
Cu1-07	1.920(3)				
Cu3-O2	1.943(3)				
P-O Bond Parameters					
Distances (Å)		Angles (deg)			
P1-O4	1.614(2)	P2-O4-P1	121.54(15)		
P2-O5	1.521(3)	O-P-O range	103.86-112.92		
P-O rest	1.500-1.510	P-O-Cu range	125.61-133.19		

Table S2. Selected bond parameters for complex 2.2CH<sub>3</sub>CN.2H<sub>2</sub>O

## **References for supporting information**

- D. D. Perrin, W. L. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, **1980**.
- [2] D. F. Evans, J. Chem. Soc., 1959, 2003
- [3] S. Sabiah, Ph.D. Thesis, Indian Institute of Technology Madras, India, October, 2007.
- [4] G. M. Sheldrick, SHELXS-86, University of Göttingen, 1986.
- [5] G. M. Sheldrick, SHELXL-97, University of Göttingen, 1997.
- [6] C.P. Nash, J. Phys. Chem. 1960, 64, 950.