## **Electronic Supporting Information**

### The Copper(II)-Phytate-Terpyridine Ternary System: The First Crystal Structures Showing the Interaction of Phytate with bivalent metal and ammonium cations<sup>†</sup>‡

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#### **General Information**

All chemicals used throughout this work were purchased from commercial sources and used without further purification. CuSO<sub>4</sub>·5H<sub>2</sub>O (Sigma-Aldrich, >98%) was used as metal source. 2,2':6'2''-terpyridine (98%) was supplied from Sigma-Aldrich. The dipotassium salt of Ins*P*<sub>6</sub>, K<sub>2</sub>H<sub>10</sub>Ins*P*<sub>6</sub>·2.5 H<sub>2</sub>O, was purchased from Sigma-Aldrich and the purity was checked by elemental and thermogravimetric analysis. Methanol, ethanol and acetone (99%) were obtained from Dorwill. All aqueous solutions were prepared with ultrapure water obtained from a Millipore-MilliQ plus system (up to 18 MΩ cm<sup>-1</sup>) and used immediately after preparation. The ionic strength was adjusted to 0.15 M with NMe<sub>4</sub>Cl (Fluka). The standard HCl solutions were prepared by diluting Merck standard ampoules. The titrant solution (0.1 M NMe<sub>4</sub>OH in 0.15 M NMe<sub>4</sub>Cl) was prepared by dissolving NMe<sub>4</sub>OH·5H<sub>2</sub>O (Fluka), and was standardized with potassium biphthalate. Cu(II) solutions were standardized according to standard techniques.<sup>1</sup>

Infrared spectroscopy was carried out on a Bomen FTIR spectrophotometer, with samples present as KBr (1%) pellets. The assignation of the most important infrared bands was carried out according to previously reported works on related systems.<sup>2-4</sup> Thermal analysis was performed on a Shimadzu DTA-50, TGA-50 instrument with a TA 50I interface, using a platinum cell and nitrogen atmosphere. Experimental conditions were 1 °C min<sup>-1</sup> temperature ramp rate and 50 mL min<sup>-1</sup> nitrogen flow rate. Elemental analysis (C, H, N) was performed on a CHNS/O Thermo Scientific FLASH 2000 instrument.

#### **Experimental Details of Potentiometric Measurements**

The chemical behavior of  $InsP_6$ -terpyridine-Cu(II) containing systems was analyzed through potentiometric titrations (*ca.* 150 experimental points each), performed for the mono, binary and ternary systems. The number of titrations, ligand and metal ion concentrations, and ligand to metal molar ratios set for the potentiometric experiments are listed in Table S1. Protonation constants values for  $InsP_6$  were taken from our previous report under identical conditions.<sup>5</sup> The formation of soluble hydroxo species of Cu(II) was determined under the same conditions, through 4 analogous potentiometric titrations in the 0.4 to 1.3 mM metal ion concentration interval. The obtained values for these hydrolysis constants ( $logK_1 = -6.80(6)$ ;  $logK_{22} = -9.50(9)$ ) were taken into account in the calculation of the formation constants of Cu(II) containing species.

In each potentiometric experiment, the solutions were poured into a 50 mL titration cell. After thermal equilibrium was reached, hydrogen ion concentrations were determined by successive readings, each performed after a small incremental addition of standard 0.1 M NMe<sub>4</sub>OH solution. The titrant addition and e.m.f. measurements were carried out using an automatic titrator Mettler-Toledo DL50-Graphix. The ionic strength was kept constant throughout the titrations by using solutions containing 0.15 M NMe<sub>4</sub>Cl and relatively low concentrations of the metal ions. Presaturated argon (free of CO<sub>2</sub>) was bubbled through the solutions during titrations and the temperature was kept at 37.0±0.1 °C. Equilibrium attainment after each titrant addition was verified by controlling the deviation of successive e.m.f. readings and performing back titrations. Independent stock solutions were used in some selected titrations to check reproducibility. The cell electrode potential  $E^{\circ}$ , and the acidic junction potential were determined from independent titrations of the strong acid with the titrant solution.<sup>6</sup> In this way, the pH scale was the free concentration scale. The calibration in the alkaline range was checked by calculating  $K_w$  values. Potentiometric data were analyzed by using the HYPERQUAD program.<sup>7</sup> The fit of the values predicted by the model to the experimental data was estimated on the basis of the  $\sigma$  parameter, corresponding to the scaled sum of square differences between predicted and experimental values. Many other possible stoichiometries were tried for each system, and final models were selected on the basis of the  $\sigma$ parameter, the model confidence level estimator, chi-square, and the internal consistency of data reflected in standard deviations of the formation constants.<sup>7</sup> Species distribution diagrams (Figures 1 and S2) were produced by using the HySS program.<sup>8</sup>

#### Synthesis of (H<sub>2</sub>terpy)<sub>3</sub>(H<sub>8</sub>InsP<sub>6</sub>)<sub>1.5</sub>·9H<sub>2</sub>O (1)

7 mg of terpyridine (0.03 mmol) was dissolved in 0.4 mL of an aqueous solution of  $K_2H_{10}InsP_6$ ·2.5 H<sub>2</sub>O (8 mg, 0.01 mmol). Then, 1.6 mL of water was added and the solution was poured into a 10 mL screw cap test tube. Compound **1** (8 mg, 62%), obtained upon diffusion of acetone into this solution at room temperature, was collected by filtration and air-dried. Found: N, 6.9; C, 34.8; H, 4.5. Calc. for ( $C_{15}H_{13}N_3$ )<sub>3</sub>( $C_6H_{14}P_6O_{24}$ )<sub>1.5</sub>·9H<sub>2</sub>O: N, 6.8; C, 35.0; H 4.2%.  $v_{max}/cm^{-1}$  3476-3409 (O–H and N–H), 3105-2833 (C–H), 1587-1289 (C–N and C–C) and 1177-954 (P–O);  $\delta_{max}/cm^{-1}$  1621-1604 (H<sub>2</sub>O), 1177-954 (C–H), 830-614 (C–C–C and C–C–N) and 513 (O–P–O);  $\rho_{max}/cm^{-1}$  830-614 (C–H). Light yellow crystals of (H<sub>2</sub>terpy)<sub>3</sub>(H<sub>8</sub>InsP<sub>6</sub>)<sub>1.5</sub>·20.5H<sub>2</sub>O suitable for X-ray analysis were obtained from an aqueous solution of **1** upon slow (two weeks) diffusion of acetone at room temperature.

#### Synthesis of (H<sub>2</sub>terpy)<sub>3</sub>(H<sub>6</sub>InsP<sub>6</sub>)·20H<sub>2</sub>O (2)

Complex 2 was prepared by dissolving terpyridine (7 mg, 0.03 mmol) and K<sub>2</sub>H<sub>10</sub>Ins*P*<sub>6</sub>·2.5 H<sub>2</sub>O (11 mg, 0.015 mmol) in 0.4 mL of water. Then, 0.6 mL of water was added. Acetone was dropwise added while stirring until a white solid precipitated. Compound **2** (8 mg, 47%) was collected by filtration and air-dried. Found: N, 7.0; C, 35.1; H, 5.0. Calc. for (C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>)<sub>3</sub>(C<sub>6</sub>H<sub>12</sub>P<sub>6</sub>O<sub>24</sub>)·20H<sub>2</sub>O: N, 7.3; C, 35.6; H, 5.3%.  $v_{max}$ /cm<sup>-1</sup> 3476-3409 (O–H and N–H), 3105-2833 (C–H), 1587-1289 (C– N and C–C) and 1177-954 (P–O);  $\delta_{max}$ /cm<sup>-1</sup> 1177-954 (C–H), 1621-1604 (H<sub>2</sub>O), 830-614 (C–C–C and C–C–N) and 513 (O–P–O);  $\rho_{max}$ /cm<sup>-1</sup> 830-614 (C–H). Light yellow crystals of (H<sub>2</sub>terpy)<sub>3</sub>(H<sub>6</sub>InsP<sub>6</sub>)·24H<sub>2</sub>O suitable for X-ray analysis were obtained from an aqueous solution of **2** upon slow (four weeks) diffusion of acetone at room temperature.

#### Synthesis of $Cu_6(InsP_6) \cdot 14H_2O$

A 0.01 M aqueous solution of Ins $P_6$  was prepared and its pH adjusted to 10 by the addition of 1 M LiOH. To 30 mL (0.3 mmol) of this solution, 0.45 g CuSO<sub>4</sub>·5H<sub>2</sub>O (1.8 mmol) dissolved in the minimum amount of water was added. A light blue solid (146 mg, 38%) immediately formed, which was separated by centrifugation, thoroughly washed with water (3 x 10 mL) then with ethanol (2 x 10 mL) and air-dried. Found: C, 5.4; H, 2.9; Cu, 29.6. Calc. for Cu<sub>6</sub>C<sub>6</sub>H<sub>34</sub>O<sub>38</sub>P<sub>6</sub>: C, 5.6; H, 2.7; Cu, 29.8%. Thermal analysis agreed with the proposed formula: 19.8% weight loss corresponding to the elimination of water, compared with a calculated value of 19.7%.  $v_{max}/cm^{-1}$  3408 (O–H), 2927-2860 (C–H), 1122 and 993 (PO<sub>2</sub><sup>-</sup>) and 852-796 (P–OH);  $\delta_{max}/cm^{-1}$  1634 (H<sub>2</sub>O) and 549 (O–P–O);  $\rho_{max}/cm^{-1}$  852-796 (PO–H).

#### Synthesis of K[Cu<sub>4</sub>(H<sub>3</sub>InsP<sub>6</sub>)(terpy)<sub>4</sub>]·26H<sub>2</sub>O (3)

4.7 mg of Cu<sub>6</sub>(Ins*P*<sub>6</sub>)·14H<sub>2</sub>O (0.004 mmol) was dissolved in a 0.4 mL aqueous solution of K<sub>2</sub>H<sub>10</sub>Ins*P*<sub>6</sub>·2.5 H<sub>2</sub>O (12 mg, 0.015 mmol). Then 1 mL of water was added. Finally, 0.5 mL solution of terpyridine (3.3 mg, 0.014 mmol) in methanol was slowly added to this solution with stirring, while a change of the solution color from light blue to dark green was observed. The pH was adjusted to 7.3 by the addition of 1 M NMe<sub>4</sub>OH, and the solution was poured into a 10 mL screw cap test tube. Dark green crystals of **3** (6.3 mg, 77%), suitable for X-ray analysis, were obtained upon diffusion of acetone into this solution, at room temperature, over four weeks. They were collected by filtration, washed with water and air-dried. Found: N, 6.9; C, 34.0; H, 4.0. Calc. for KCu<sub>4</sub>(C<sub>6</sub>H<sub>9</sub>P<sub>6</sub>O<sub>24</sub>)(C<sub>15</sub>H<sub>11</sub>N<sub>3</sub>)<sub>4</sub>·26H<sub>2</sub>O: N, 7.2; C, 33.8; H, 4.5%.  $v_{max}$ /cm<sup>-1</sup> 3404 (O–H), 3078-2980 (C–H), 1597-1406 (C–N and C–C) and 1194-974 (P–O);  $\delta_{max}$ /cm<sup>-1</sup> 1655 (H<sub>2</sub>O), 1330-1256 (C–H) and 523 (O–P–O);  $\rho_{max}$ /cm<sup>-1</sup> 829-731 (C–H).

#### Synthesis of [Cu<sub>2</sub>(H<sub>8</sub>InsP<sub>6</sub>)(terpy)<sub>2</sub>]·7.5H<sub>2</sub>O (4)

28 mg of Cu<sub>6</sub>(Ins*P*<sub>6</sub>)·14H<sub>2</sub>O (0.022 mmol) was dissolved in a 0.4 mL aqueous solution of K<sub>2</sub>H<sub>10</sub>Ins*P*<sub>6</sub>·2.5 H<sub>2</sub>O (72 mg, 0.092 mmol). Then 13 mL of water was added. Finally, 3 mL of a solution of terpyridine (20 mg, 0.086 mmol) in methanol was slowly added with stirring, while a change of the solution color from light blue to dark green was observed. After three weeks, dark aquamarine crystals of **4** (43 mg, 74%) were obtained by slow solvent evaporation at room temperature, and were collected by filtration and air-dried. Found: N, 6.2; C, 31.9; H, 3.6. Calc. for Cu<sub>2</sub>(C<sub>6</sub>H<sub>14</sub>P<sub>6</sub>O<sub>24</sub>)(C<sub>15</sub>H<sub>11</sub>N<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O: N, 6.2; C, 31.8; H, 3.6%.  $v_{max}$ /cm<sup>-1</sup> 3423 (O–H), 3121-2995 (C–H), 1577-1409 (C–N and C–C) and 1220-949 (P–O);  $\delta_{max}$ /cm<sup>-1</sup> 1601 (H<sub>2</sub>O), 1330-1258 (C–H) and 507 (O–P–O);  $\rho_{max}$ /cm<sup>-1</sup> 829-733 (C–H).

Crystals of  $[Cu_2(H_8InsP_6)(terpy)_2]$ ·7.5H<sub>2</sub>O suitable for X-ray analysis were obtained by slow evaporation at room temperature of the mother liquor collected after recovery of the above crystals of  $Cu_2(C_6H_{14}P_6O_{24})(C_{15}H_{11}N_3)_2$ ·6H<sub>2</sub>O.

In the case of compounds **1-3**, several attempts to prepare crystals of the complex suitable for X-ray analysis were performed. The reported procedure represents the best results which gives crystals of modest quality.

#### Structural refinement details

#### (H<sub>2</sub>terpy)<sub>3</sub>(H<sub>8</sub>InsP<sub>6</sub>)<sub>1.5</sub>·20.5H<sub>2</sub>O (1)

Crystals were of poor quality and gave very low intensity data at high resolution. As a consequence data were collected only up to 0.9. Anisotropic displacement parameters were used for all the non-hydrogen atoms, while hydrogen atoms were introduced in calculated position linked to all the carbon atoms and the nitrogen atoms of the two external pyridine rings per each terpyridine molecule. All the hydrogen were isotropically refined with fixed thermal parameter (U = 0.05 Å<sup>2</sup>). Terpyridine molecules are affected by different degree of disorder and the ADPs of some carbon atoms were restrained to assume an isotropic behavior. Moreover, two phenyl rings of one terpyridine were found in double positions. A very high solvent content was found around the phytate anions. 30 water oxygen atoms were found in the asymmetric unit (60 in the unit cell) and refined with partial occupancy factors. No hydrogen atom was located in the  $\Delta$ F map for the ligands nor for the water molecules.

#### (H<sub>2</sub>terpy)<sub>3</sub>(H<sub>6</sub>InsP<sub>6</sub>)·24H<sub>2</sub>O (2)

Crystals were of poor quality and gave very low intensity data at high resolution. As a consequence data were collected only up to 0.9. Anisotropic displacement parameters were used for all the non-hydrogen atoms, while hydrogen atoms were introduced in calculated position linked to all the carbon atoms and the nitrogen atoms of the two external pyridine rings of each terpyridine molecule. All the hydrogen were refined with isotropic thermal parameter calculated in agreement with the linked atom. A very high solvent content was found around the phytate anions. 30 water oxygen atoms were found in the asymmetric unit (120 in the unit cell) and refined with partial occupancy factors. No hydrogen atom was located in the  $\Delta F$  map for the ligands nor for the water molecules, and the ADPs of two water molecules were restrained to the isotropic behavior.

#### K[Cu<sub>4</sub>(H<sub>3</sub>InsP<sub>6</sub>)(terpy)<sub>4</sub>]·26H<sub>2</sub>O (3)

Anisotropic displacement parameters were used for all the non-hydrogen atoms, while hydrogen atoms were introduced in calculated position linked to the carbon atoms. All the hydrogens were refined with isotropic thermal parameter calculated in agreement with the linked atom. A very high solvent content was found around the phytate anion. 30 water oxygen atoms were found in the asymmetric unit (60 in the unit cell) and refined with partial occupancy factors. No hydrogen atom was located in the  $\Delta$ F map for the water molecules. One of the terpyridine molecule was affected by disorder and the ADPs of its carbon and nitrogen atoms were restrained to the isotropic behavior.

#### $[Cu_2(H_8InsP_6)(terpy)_2]$ ·7.5H<sub>2</sub>O (4)

Anisotropic displacement parameters were used for all the non-hydrogen atoms, while hydrogen atoms were introduced in calculated position and their coordinates and site occupancy factor were refined accordingly to the linked carbon atoms. No hydrogen atom was located in the  $\Delta F$  map for water molecules.

	System				
Component	(number of titrations)				
Concentration range (mM)	terpyridine-H <sup>+</sup> (3)	terpyridine-Cu(II) (4)	InsP <sub>6</sub> -Cu(II) (7)	Ins <i>P</i> <sub>6</sub> - terpyridine (6)	InsP <sub>6</sub> -terpyridine-Cu(II) (8)
Cu(II)		1.3 – 2.6	0.4 - 1.3		1.3 – 5.0
InsP <sub>6</sub>			0.4 - 4.0	0.9 – 1.5	0.3 – 1.3
terpyridine	1.1 – 2.1	1.4 - 2.9		1.0 - 2.9	1.0 - 3.9
Molar ratio					
InsP <sub>6</sub> /Cu(II)			1.0 - 5.0		0.26 - 1.0
terpyridine/Cu(II)		0.5 – 2.2			0.5 - 1.0
InsP <sub>6</sub> /terpyridine				0.3 - 1.0	0.25 - 1.0

 Table S1. Experimental conditions applied for the potentiometric titrations.

System	pgrs	$\log \beta_{\rm pars}$	σ
	0101	4.637(7)	
Terpyridine	0102	8.13(1)	0.54
	0103	10.01(6)	
$O^{2+1}_{-1}$	100-1	-6.80(6)	0.02
Cu <sup>2+</sup> hydrolysis	200-2	-9.50(9)	0.03
	1100	8.84(6)	
Cu <sup>2+</sup> -terpyridine	1200	15.27(6)	0.42
	220-2	4.4(1)	
	1012	30.19(4)	
$C^{2+}$ I	1013	38.10(2)	0.24
$Cu^2$ - Ins $P_6$	1014	44.5(1)	0.34
	5012	50.37(5)	
	0112	24.46(6)	
	0113	35.51(3)	
	0114	45.06(3)	
	0115	52.29(4)	
	0116	58.11(4)	0.29
т <sup>.</sup> 1, тр	0117	62.64(5)	
Terpyridine-InsP <sub>6</sub>	0118	66.28(5)	
	0119	69.32(6)	
	0215	54.94(5)	
	0216	60.81(6)	
	0217	65.59(5)	
	0218	69.86(6)	
	1112	36.34(2)	
	1113	46.15(3)	
	1114	54.88(3)	
	1115	61.56(5)	
	1116	66.94(6)	
	1117	70.17(7)	
Cus2+ tomorniding IngD	1118	72.35(9)	0.70
Cu <sup>2</sup> -terpyrialite-IIIsP <sub>6</sub>	2114	59.78(6)	0.78
	2213	59.46(5)	
	2214	66.97(6)	
	3214	72.80(5)	
	3313	72.51(4)	
	4411	67.28(4)	
	4412	76.25(8)	

**Table S2**. Logarithms of the overall equilibrium constants for the formation of  $Cu_p(terpyridine)_q(InsP_6)_rH_s$  species, in 0.15 M NMe<sub>4</sub>Cl at 37.0 °C.

 $\sigma$  represents the scaled sum of square differences between predicted and experimental values. Values given in parentheses are the 1 $\sigma$  statistical uncertainties in the last digit of the constant. **Table S3.** Crystal data and structure refinement for  $(H_2 terpy)_3(H_8 InsP_6)1.5 \cdot 20.5 H_2O$  (1), $(H_2 terpy)_3(H_6 InsP_6) \cdot 24 H_2O$ (2), $K[Cu_4(H_3 InsP_6)(terpy)_4] \cdot 26 H_2O$ (3),and $[Cu_2(H_8 InsP_6)(terpy)_2] \cdot 7.5 H_2O$  (4).

	(1)	(2)	(3)	(4)
Empirical formula	$C_{54}H_{101}N_9O_{56.5}P_9$	$C_{51}H_{99}N_9O_{48}P_6$	$C_{66}H_{105}Cu_4KN_{12}O_{50}P_6$	$C_{36}H_{51}Cu_2N_6O_{31.5}P_6$
Formula weight	2059.17	1792.21	2345.70	1384.73
Temperature (K)	150	100	100	150
space group	P -1	P 2 <sub>1</sub> /n	P-1	P-1
a (Å)	16.001(1)	10.2007(3)	13.1214(6)	13.0134(6)
b (Å)	16.367(1)	26.3327(7)	14.4167(5)	14.0376(6)
c (Å)	17.493(1)	29.1253(8)	24.5355(9)	15.1132(8)
α (°)	99.447(6)	90.00	95.333(3)	108.626(4)
β (°)	92.632(5)	97.695(3)	91.597(4)	98.790(4)
γ (°)	103.483(5)	90.00	96.973(4)	95.209(4)
Volume (Å <sup>3</sup> )	4377.3(5)	7753.0(4)	4583.4(3)	2556.6(2)
Ζ	2	4	2	2
Independent reflections / R(int)	6005 / 0.0472	6243 / 0.1162	16448 / 0.0743	9532 / 0.0512
μ (mm <sup>-1</sup> )	2.676 (Cu-ka)	2.274(Cu-ka)	3.396(Cu-ka)	3.763(Cu-ka)
R indices $[I>2\sigma(I)]^*$	R1 = 0.1164	R1 = 0.0471	R1 = 0.0806	R1 = 0.0559
[ (-)]	wR2 = 0.2995	wR2 = 0.0807	wR2 = 0.2043	wR2 = 0.1367
R indices (all data)*	R1 = 0.1875	R1 = 0.0619	R1 = 0.1276	R1 = 0.1029
/	wR2 = 0.3716	wR2 = 0.0861	wR2 = 0.2434	wR2 = 0.1738

\* R1 =  $\Sigma \parallel \text{Fo} \mid - |\text{Fc}| \mid / \Sigma \mid \text{Fo} \mid$ ; wR2 = [ $\Sigma \text{ w}(\text{Fo2} - \text{Fc2}) 2 / \Sigma \text{ wFo4}]^{1/2}$ 

**Table S4**. Selected bond lengths (Å) and angles (°) for  $K[Cu_4(H_3InsP_6)(terpy)_4]$ ·26H<sub>2</sub>O – e.s.d in parenthesis.

Cu1	OW3	2.201(5)
Cul	N1	2.033(6)
Cul	N2	1.944(6)
Cul	N3	2.046(6)
Cu1	O52	1.906(5)
Cu2	OW1	2.195(6)
Cu2	N4	2.036(8)
Cu2	N5	1.911(5)
Cu2	N6	2.033(6)
Cu2	P5	2.916(2)
Cu2	O53	1.957(5)
Cu3	N7	2.052(6)
Cu3	N8	1.936(6)
Cu3	N9	2.045(6)
Cu3	O23	2.174(5)
Cu3	O34	1.912(5)
Cu4	N10	2.032(7)
Cu4	N11	1.957(7)
Cu4	N12	2.028(7)
Cu4	O14	1.922(6)
Cu4	O24	2.205(5)
K1	OW2	2.832(9)
K1	012	2.736(6)
K1	O53	2.888(6)
K1	061	2.868(5)
K1	062	2.973(6)
K1	OW14	2.84(1)

-			
OW3	Cu1	N1	98.0(2)
OW3	Cu1	N2	108.3(2)
OW3	Cu1	N3	92.5(2)
OW3	Cu1	052	99.3(2)
N1	Cu1	N2	79.6(2)
N1	Cu1	N3	159.0(2)
N1	Cu1	052	91.5(2)
N2	Cu1	N3	79.9(2)
N2	Cu1	052	151.9(2)
N3	Cu1	052	104.7(2)
OW1	Cu2	N4	96.1(3)
OW1	Cu2	N5	109.1(2)
OW1	Cu2	N6	88.9(2)
OW1	Cu2	P5	122.4(2)
OW1	Cu2	053	95.0(2)
N4	Cu2	N5	80.9(3)
N4	Cu2	N6	158.6(3)
N4	Cu2	P5	101.0(2)

N4	Cu2	053	97.4(3)
N5	Cu2	N6	77.8(2)
N5	Cu2	P5	127.7(2)
N5	Cu2	053	155.9(2)
N6	Cu2	P5	93.7(2)
N6	Cu2	O53	103.0(2)
P5	Cu2	053	28.8(2)
N7	Cu3	N8	79.5(2)
N7	Cu3	N9	157.5(2)
N7	Cu3	O23	95.0(2)
N7	Cu3	O34	99.6(2)
N8	Cu3	N9	80.1(2)
N8	Cu3	O23	93.1(2)
N8	Cu3	O34	163.2(2)
N9	Cu3	O23	95.6(2)
N9	Cu3	O34	97.2(2)
O23	Cu3	O34	103.7(2)
N10	Cu4	N11	79.5(3)
N10	Cu4	N12	158.6(3)
N10	Cu4	014	102.1(3)
N10	Cu4	024	94.4(2)
N11	Cu4	N12	79.3(3)
N11	Cu4	014	147.6(3)
N11	Cu4	024	94.6(2)
N12	Cu4	014	94.3(3)
N12	Cu4	O24	90.1(2)
014	Cu4	O24	117.2(2)
OW2	K1	012	101.1(2)
OW2	K1	053	89.4(2)
OW2	K1	061	171.3(2)
OW2	K1	O62	139.6(2)
OW2	K1	W14	72.1(3)
012	K1	053	99.1(2)
012	K1	061	74.6(2)
012	K1	O62	106.6(2)
012	K1	W14	166.4(3)
053	K1	O61	83.9(2)
053	K1	O62	114.0(2)
053	K1	W14	69.7(3)
O61	K1	O62	48.9(2)
O61	K1	W14	110.5(3)
062	K1	W14	85.4(3)

**Table S5.** Selected bond lengths (Å) and angles (°) for  $[Cu_2(H_8InsP_6)(terpy)_2]$ ·7.5H<sub>2</sub>O – e.s.d in parenthesis.

Cu1	N1	2.027(6)
Cu1	N2	1.949(5)
Cu1	N3	2.031(6)
Cu1	013	1.917(4)
Cu1	O24	2.174(4)
Cu2	N4	2.034(6)
Cu2	N5	1.934(5)
Cu2	N6	2.029(6)
Cu2	014	1.906(4)
Cu2	O32'	2.144(4)

N1	Cu1	N2	79.8(2)
N1	Cu1	N3	157.8(2)
N1	Cu1	013	97.1(2)
N1	Cu1	O24'	101.9(2)
N2	Cu1	N3	79.6(2)
N2	Cu1	013	161.2(2)
N2	Cu1	O24'	98.6(2)
N3	Cu1	013	99.7(2)
N3	Cu1	O24	89.4(2)
013	Cu1	O24'	100.2(2)
N4	Cu2	N5	79.9(2)
N4	Cu2	N6	159.9(2)
N4	Cu2	O14	102.1(2)
N4	Cu2	O32'	96.5(2)
N5	Cu2	N6	80.2(2)
N5	Cu2	O14	156.7(2)
N5	Cu2	O32'	104.4(2)
N6	Cu2	014	95.0(2)
N6	Cu2	O32'	91.3(2)









scyllo-



neo-

epi-









muco-



L-chiro-

cis-





allo-



**Figure S1.** The inositol stereoisomers with hydroxyls omitted (a). Structures of  $InsP_6$  for (b) 1 axial-5 equatorial (1a5e) and (c) 5 axial-1 equatorial (5a1e) conformations.

Adapted from: R. Parthasarathy, F. Eisenberg Jr, Biochemistry, stereochemistry, and nomenclature of the inositol phopshates, in *Inositol Phosphates and Derivatives: Synthesis, Biochemistry and Therapeutic Potential*, ed. A. B. Reitz, American Chemical Society, Washington, DC, 1990, pp. 1-19.



**Figure S2.** Species distribution diagrams for terpyridine (a),  $Cu^{2+}$ -terpyridine (b),  $Cu^{2+}$ -Ins $P_6$  (c), and terpyridine-Ins $P_6$  (d) systems, in 0.15 M NMe<sub>4</sub>Cl at 37.0 °C. Ligands and metal ion concentrations are 1 mM. Ins $P_6$  is represented as L<sup>12-</sup>. (a) and (d), percentages relative to L; (b) and (c), percentages relative to Cu<sup>2+</sup>.





**Figure S3**. (a) NH···O interactions between phytate anions in *myo*-configuration and diprotonated terpyridine cations and (b) CH···O interactions between phytate anions in *scyllo*-configuration and diprotonated terpyridine cations in  $(H_2 \text{terpy})_3(H_8 \text{Ins}P_6)_{1.5} \cdot 20.5 \text{H}_2\text{O}$ .



**Figure S4.** Infinite tapes formed by alternating 18- and 20-membered rings in the  $[Cu_2(H_8InsP_6)(terpy)_2]$ ·7.5H<sub>2</sub>O (4) crystal structure (not coordinated water molecules omitted for clarity).

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