Supplementary Information

Single-crystal to single-crystal transformations in discrete hydrated dimeric copper complexes

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Experimental

Materials and Instrumentation. The commercially available starting materials, Cu(OC(=O)CH₃)₂·2H₂O, 2-(2-hydroxyethyl)pyridine (hep-H), n-propionic acid and reagent grade solvents: methanol, ethanol, isopropanol, acetonitrile, dichloromethane and N,N′-dimethylformamide were used as received. Elemental analyses were carried out with a Perkin-Elmer 240C elemental analyzer. FT-IR spectra of complexes as KBr pellets and DTA/TGA experiments were done on a Nicolet spectrophotometer and Perkin Elmer Instrument, respectively. X-ray (powder) diffraction data were collected on a Philips X'Pert Pro X-ray diffraction system using monochromated CuKα1 radiation (λ = 1.5406 Å). The magnetic susceptibility measurements at 298 K were performed using a Faraday balance (Cahn Instruments Inc., serial no. 76240).

Synthesis of [(OAc)Cu(μ-hep)₂Cu(OAc)]·2H₂O (1.2H₂O). A solution of hep-H (0.123 g, 1 mmol) in methanol (25 cm³) was added to a solution of Cu(OC(=O)CH₃)₂·2H₂O (0.199 g, 1 mmol) in methanol (25 cm³) and the resultant solution in a 100 cm³ beaker was stirred magnetically for 6 h at 298 K. The solution was then passed through the filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was then allowed to stand at 298 K for crystallization. On slow evaporation of the solvent the dark blue single crystals of 1.2H₂O were obtained after a week. M.P.: 223-225°C. Yield: 0.165 g (80%). Elemental Analalysis (%) calculated for C₉H₁₅N₁O₅Cu₁, (Mr = 280.77): C, 43.42; H, 4.97; N, 4.61. Found: C, 43.57; H, 5.01; N, 4.66. IR (KBr, cm⁻¹): 3448(br), 3080(vw), 2951(vw), 2876(w), 2830(w), 2380(vw), 2681(vw), 1590(vs), 1484(s), 1394(s), 1335(s), 1160(w), 1380(vs), 1340(m), 1315(w), 1220(w), 1112(m), 1081(s), 1056(m), 1080(m), 880(w), 779(m), 680(m), 623(m), 579(w). TGA: Temperature range °C (% Weight loss): 50-130 (5.0); 130-270 (60.5).
SCSC-transformation of [(OAc)Cu(μ-hep)_2Cu(OAc)]·2H_2O (1.2H_2O) to [(OAc)Cu(μ-hep)_2Cu(OAc)] (1). Blue coloured single crystal of 1.2H_2O was exposed to heating at 110 °C for 3 h. Subsequently the crystal was subjected to X-ray analysis which confirmed the identity of the crystal as a dehydrated [(OAc)Cu(μ-hep)_2Cu(OAc)] (1). Similar thermal method was followed to prepare the bulk sample of 1. M.P.: 217-219°C. Elemental Analysys (%) calculated for C_{18}H_{22}N_{2}O_{6}Cu_{2}, (Mr = 489.46): C, 44.26; H, 4.54; N, 5.74. Found: C, 44.37; H, 4.64; N, 5.67. IR (KBr, cm\(^{-1}\)): 3084(m), 2953(m), 2876(m), 2829(m), 2687(w), 1616(vs), 1584(vs), 1474(s), 1386(s), 1332(s), 1244(m), 1079(s), 1041(s), 876(s), 767(s), 690(s), 614(s). TGA: Temp. range °C (% Weight loss): 130-265 (64.7).

Backward SCSC-transformation of [(OAc)Cu(μ-hep)_2Cu(OAc)] (1) to [(OAc)Cu(μ-hep)_2Cu(OAc)]·2H_2O (1.2H_2O). Single-crystal of (1) was taken in a small vial (3 inches length and 0.5 inch width) which was then placed inside one bigger vial (3.5 inches length and 1 inch width) containing 2 cm\(^3\) water and the outer vial was closed. The crystal was allowed to stand in presence of water vapour at 298K for 24 h. The crystal was then subjected to X-ray diffraction data collection which confirmed the regeneration of the dihydrated 1.2H_2O. The Bulk sample was then prepared by following the same above method. M.P.: 223-225°C. Yield: 165 mg (80%). Elemental Analysys (%) calculated for C_{9}H_{15}N_{1}O_{5}Cu_{1}, (Mr = 280.77): C, 43.42; H, 4.97; N, 4.61. Found: C, 43.50; H, 5.04; N, 4.56. IR (KBr, cm\(^{-1}\)): 3448(br), 3082(vw), 2951(vw), 2876(w), 2830(m), 2360(vw), 1591(vs), 1484(s), 1396(vs), 1336(s), 1248(w), 1198(w), 1168(w), 1117(m), 1081(s), 925(vw), 882(vw), 780(m), 680(m), 623(s), 580(vw). TGA: Temperature range °C (% Weight loss): 50-130 (5.3); 130-250 (57).

Synthesis of [(OAc)Cu(μ-hep)_2Cu(O^nPr)]·2H_2O (2.2H_2O). A solution of 1.2H_2O (0.250 g, 0.5 mmol) in 25 cm\(^3\) methanol was taken in a 100 cm\(^3\) beaker. Propionic acid (CH\(_3\)CH\(_2\)COOH,
0.02 cm³, 0.25 mmol) was added to the above solution of 1.2H₂O and the resultant solution was stirred for 6 h at room temperature. The solution was allowed to stand at room temperature for crystallization. Dark blue single crystals of 2.2H₂O were obtained within 10 days by slow evaporation of the solvent. M.P.: 228-230°C. Yield: 0.175 g (70 %). Elemental Analysis (%) calculated for C₁₀H₂₈N₂O₈Cu₂, (Mr = 539.51): C, 42.38; H, 5.24; N, 5.21. Found: C, 42.47; H, 5.21; N, 5.26. IR (KBr, cm⁻¹): 3448(br), 3081(vw), 2955(vw), 2879(w), 2821(w), 2361(vw), 1608(vs), 1591(vs), 1485(s), 1447(vw), 1394(s), 1360(vw), 1334(vw), 1314(vw), 1281(w), 1248(w), 1115(m), 1081(s), 1051(w), 1028(vw), 880(m), 776(m), 680(w), 625(m), 579(w).

TGA: Temperature range °C (% Weight loss): 25-90 (7.0); 90-272 (62.4).

**SCSC-transformation of \[(OAc)Cu(µ-hep)₂Cu(O₉Pr)]·2H₂O (2.2H₂O) to \[(OAc)Cu(µ-hep)₂Cu(O₉Pr)] (2).** Blue coloured single crystal of 2.2H₂O was exposed to heating at 110 °C for 3 h. The crystal was then subjected to X-ray analysis which confirmed the identity of the crystal as a dehydrated \[(OAc)Cu(µ-hep)₂Cu(O₉Pr)] (2). Similarly the bulk sample of 2 was prepared. M.P: 219-221°C. Elemental Analysis (%) calculated for C₁₀H₂₄N₂O₆Cu₂ (Mr = 503.48): C, 45.42; H, 4.82; N, 5.58. Found: C, 45.37; H, 4.64; N, 5.67. IR (KBr, cm⁻¹): 3081(vw), 2924(vw), 2879(vw), 2854(vw), 2360(m), 2341(m), 1609(vs), 1592(vs), 1485(m), 1394(s), 1360(vw), 1282(w), 1249(w), 1116(w), 1082(m), 1051(vw), 1028(vw), 879(m), 776(m), 679(w), 621(s). TGA: Temp. range °C (% Weight loss): 200-265 (55.7).

**Backward SCSC-transformation of \[(OAc)Cu(µ-hep)₂Cu(O₉Pr)] (2) to \[(OAc)Cu(µ-hep)₂Cu(O₉Pr)]·2H₂O (2.2H₂O).** Single-crystal of (2) inside one small vial (3 inches length and 0.5 inch width) was placed inside another bigger vial (3.5 inches length and 1 inch width) containing 2 mL water and the outer vial was closed. The single crystal was allowed to stand in presence of water vapour at 298K for 24 h and subsequently the crystal was subjected to X-ray...
diffraction study which established the regeneration of the parent dihydrated 2.2H₂O. The same method was also followed to regenerate the bulk sample of the dihydrated 2.2H₂O from 2. M.P.: 228-230°C Elemental Analaysis (%) calculated for C₁₉H₂₈N₂O₈Cu₂, (Mr = 539.51): C, 42.38; H, 5.24; N, 5.21. Found: C, 42.43; H, 5.22; N, 5.24. IR (KBr, cm⁻¹): 3447(br), 2953(vw), 2929(w), 2878(w), 2851(w), 2820(w), 2356(m), 2334(w), 1611(vs), 1588(vs), 1483(s), 1395(s), 1333(vw), 1280(w), 1247(w), 1114(m), 1079(s), 1052(w), 882(m), 791(w), 777(m), 679(w), 622(m), 577(vw). TGA: Temperature range °C (% Weight loss): 25-90 (7.0); 170-272 (62.4).

The transformations of 1.2H₂O → 1 and 2.2H₂O → 2 were taken place without any change in colour.

Synthesis of [(O₉Pr)Cu(µ-hep)₂Cu(O₉Pr)]⋅2H₂O (3.2H₂O). Propionic acid (0.04 cm³, 0.5 mmol) was added to the preformed 1.2H₂O in 25 cm³ MeOH (0.250 g, 0.5 mmol) and the resultant solution was stirred magnetically for 6 h at 298 K. The subsequent slow evaporation of the solution yielded the dark blue single crystals of 3.2H₂O within 10 days. M.P.: 229-231°C. Yield: 0.140 g (70 %). Elemental Analaysis (%) calculated for C₂₀H₃₀N₂O₈Cu₂, (Mr = 553.54): C, 43.47; H, 5.48; N, 5.07. Found: C, 43.50; H, 5.42; N, 5.00. IR (KBr, cm⁻¹): 3404(br), 3082(w), 3036(vw), 2971(m), 2892(vw), 2837(m), 2687(vw), 1616(vs), 1586(s), 1474(m), 1414(s), 1392(s), 1271(s), 1123(m), 1068(s), 977(w), 880(s), 776(s), 626(s), 579(w). TGA: Temperature range °C (% Weight loss): 25-97 (7.0); 100-246 (60).

Irreversible SCSC-transformation of [(O₉Pr)Cu(µ-hep)₂Cu(O₉Pr)]⋅2H₂O (3.2H₂O) to [Cu₄(µ₃-hep)₂(µ-hep)₂(µ-O₉Pr)₂(O₉Pr)₂] (4). Blue coloured single crystal of 3 was exposed to heating at 110 °C for 3 h which led to the distinct change in colour of the crystal from blue to green without the loss in crystallinity. X-ray analysis of the green crystal confirmed its identity as a double open cubane tetrameric structure of [Cu₄(µ₃-hep)₂(µ-hep)₂(µ-O₉Pr)₂(O₉Pr)₂] (4).
Similar thermal method was subsequently followed to prepare the bulk sample of 4. M.P: 237-238°C. Elemental Analalysis (%) calculated for C₄₀H₅₂N₄O₁₂Cu₄, (Mr = 1035.02): C, 46.51; H, 5.08; N, 5.43. Found: C, 46.57; H, 5.04; N, 5.48. IR (KBr, cm⁻¹): 3129(vw), 3072(vw), 3037(vw), 2964(w), 2937(w), 2842(w), 1611(vs), 14856(m), 1445(m), 1370(vs), 1266(s), 1118(m), 1069(m), 871(m), 762(m). TGA: Temp. range °C (% Weight loss): 150-280 (68).

**Alternative vapour diffusion method for the SCSC-transformation of [(O°Pr)Cu(μ-hep)₂Cu(O°Pr)₂H₂O (3.2H₂O) to [Cu₄(μ₃-hep)₂(μ-hep)₂(μ-O°Pr)₂(O°Pr)₂] (4).** Blue coloured single crystal of 3.2H₂O was taken in a small sample glass vial (3 inches length and 0.5 inch width) which was placed inside a bigger bottle (3.5 inches length and 1 inch width) containing 2 mL methanol. The outer bottle was closed and the set up was left at room temperature over a period of 5 m which led to the distinct change in colour of the crystal from blue to green with retaining the crystallinity. The green crystal was then subjected to X-ray analysis which confirmed the identity of the crystal as a double open cubane tetrameric structure of [Cu₄(μ₃-hep)₂(μ-hep)₂(μ-O°Pr)₂(O°Pr)₂] (4). The SCSC transformation of 3.2H₂O to 4 was also checked in presence vapour of different solvents (Figure A).

Similar vapour diffusion method was also followed to prepare the bulk sample of 4. M.P: 237-238°C. Elemental Analalysis (%) calculated for C₄₀H₅₂N₄O₁₂Cu₄, (Mr = 1035.02): C, 46.51; H, 5.08; N, 5.43. Found: C, 46.54; H, 5.03; N, 5.40. IR (KBr, cm⁻¹): 3129(vw), 3072(vw), 3037(vw), 2964(w), 2937(w), 2904(w), 2844(w), 1616(vs), 14896(m), 1441(m), 1392(vs), 1266(s), 1114(m), 1063(m), 1036(m), 877(m), 762(m), 603(m). TGA: Temp. range °C (% Weight loss): 150-280 (68).
Blue crystals of 3.2H₂O

Vapour diffusion technique

Green crystals of 4

Fig. A Photographs of the transformation of 3.2H₂O to 4 using vapour diffusion technique in different solvents
X-ray crystallography

Single crystal X-ray structural studies of all the crystals were performed on a CCD Oxford Diffraction XCALIBUR-S diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 150(2) K using graphite-monochromated Mo Kα radiation ($\lambda_{\alpha} = 0.71073$ Å). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct method using SHELXS-97 and refined by full matrix least squares with SHELXL-97, refining on $F^2$.¹

The positions of all the atoms were obtained by direct method. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of water molecules were generated through Fourier peaks for 1.2H$_2$O, 1.2H$_2$O(Regenerated). The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factor, generally 1.2 x $U_{eq}$ of their parent atoms. All the H-bonding interactions, mean plane analyses, and molecular drawings were obtained using the ORTEP program. The selective crystal and refinement data, bond distances and bond angles and hydrogen bond parameter are summarized in Tables S1-S3, Table S4 and Table S5, respectively. In 1.2H$_2$O (initial as well as regenerated) the asymmetric unit contains half of the complex molecule and two lattice water molecules thus the overall molecular formula is taken by considering $z = 2$ with centrosymmetric Pī space group. The disordered methyl groups, C20/C20’ in 4, obtained either by heating or by vapour diffusion are having double occupancy ratios of 55:45% or 53:47%, respectively.

Table S1  Selected crystallographic parameters for 1.2H₂O, 1 and regenerated 1.2H₂O.

<table>
<thead>
<tr>
<th></th>
<th>1.2H₂O (150K)</th>
<th>1 (150K)</th>
<th>Regenerated(150K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₉H₁₅N₁O₅Cu₁</td>
<td>C₁₈H₂₂N₂O₆Cu₂</td>
<td>C₉H₁₅N₁O₅Cu₁</td>
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<td>489.46</td>
<td>280.77</td>
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<td>Crystal symmetry</td>
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<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pī</td>
<td>Pī</td>
<td>Pī</td>
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<td>7.702(3)</td>
<td>7.900(3)</td>
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<tr>
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<td>8.943(3)</td>
<td>8.684(3)</td>
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<tr>
<td>c /Å</td>
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<td>8.698(4)</td>
<td>10.058(4)</td>
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<tr>
<td>α /º</td>
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<td>100.46(4)</td>
<td>71.77(3)</td>
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<td>β /º</td>
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<td>106.16(4)</td>
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<td>γ /º</td>
<td>69.45(3)</td>
<td>93.14(4)</td>
<td>69.51(3)</td>
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<td>290</td>
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<td>Crystal size mm³</td>
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<td>0.38 x 0.34 x 0.32</td>
<td>0.33 x 0.26 x 0.21</td>
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<td>θ range(deg)</td>
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<td>3.14 to 25.00</td>
<td>3.16 to 25.00</td>
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<td>Reflections collected</td>
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<td>4327 / 1748 [R(int) = 0.0291]</td>
<td>5298 / 2145 [R(int) = 0.1173]</td>
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<td>/ unique</td>
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<td>1748 / 0 / 128</td>
<td>2145 / 24 / 162</td>
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<td>Data / restraints /</td>
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<td>0.0271, 0.0692</td>
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<td>0.897 and -0.987</td>
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<td>peak/hole, (e Å⁻³)</td>
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<td>737391</td>
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Table S2  Selected crystallographic parameters for $2.2\text{H}_2\text{O}$, 2 and regenerated $2.2\text{H}_2\text{O}$.

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<th>$2.2\text{H}_2\text{O}$ (150K)</th>
<th>2 (150K)</th>
<th>2.2H$_2$O Regenerated(150K)</th>
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<td><strong>Empirical formula</strong></td>
<td>C$<em>{19}$ H$</em>{28}$ N$_2$ O$_8$ Cu$_2$</td>
<td>C$<em>{19}$ H$</em>{24}$ N$_2$ O$_6$ Cu$_2$</td>
<td>C$<em>{19}$ H$</em>{28}$ N$_2$ O$_8$ Cu$_2$</td>
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<td>503.48</td>
<td>539.51</td>
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<td><strong>Crystal symmetry</strong></td>
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<td>Triclinic</td>
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<tr>
<td><strong>Space group</strong></td>
<td>Pī</td>
<td>Pī</td>
<td>Pī</td>
</tr>
<tr>
<td><strong>a /Å</strong></td>
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<td>7.855(2)</td>
<td>7.8434(14)</td>
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<td>10.137(3)</td>
<td>10.2268(12)</td>
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<tr>
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<td>15.6326(8)</td>
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<tr>
<td><strong>α /⁰</strong></td>
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<td>75.74(3)</td>
<td>76.83(3)</td>
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<tr>
<td><strong>β /⁰</strong></td>
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<td>85.36(3)</td>
<td>77.201(14)</td>
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<td><strong>Reflections collected</strong></td>
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<td>6443 / 3366 [R(int) = 0.0565]</td>
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<td><strong>R1, wR2 [I &gt; 2σ(I)]</strong></td>
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<td>0.0566, 0.1111</td>
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<td><strong>R1, wR2(all data)</strong></td>
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<td><strong>GOF</strong></td>
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<td>1.072</td>
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<td><strong>Largest diff. peak/hole, (e Å⁻³)</strong></td>
<td>1.168 and -0.343</td>
<td>0.853 and -0.451</td>
<td>1.212 and -0.866</td>
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<td><strong>CCDC No.</strong></td>
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Table S3  Selected crystallographic parameters for 3.2H₂O and 4.

<table>
<thead>
<tr>
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<th>3.2H₂O (150K)</th>
<th>4 by Heating(150K)</th>
<th>4 by Vapour diffusion (150K)</th>
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</thead>
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<tr>
<td>Empirical formula</td>
<td>C₂₀ H₃₀ N₂ O₈ Cu₂</td>
<td>C₄₀ H₅₂ N₄ O₁₂ Cu₄</td>
<td>C₄₀ H₅₂ N₄ O₁₂ Cu₄</td>
</tr>
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Table S4  Selected bond distances (Å) and bond angles (°).

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<th>2</th>
<th>2.2H₂O (Regenerated)</th>
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<th>4-Heating</th>
<th>4-Vapour diffusion</th>
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Table S5  Hydrogen bonding parameters (Å, °).

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1.2H₂O

| C(2)-H(2)...O(3)#2 | 0.95 | 2.48 | 3.388(12) | 159.5 |
| C(4)-H(4)...O(3)#3 | 0.95 | 2.31 | 2.804(2) | 141.9 |
| O(111)-H(111)...O(1)#1 | 0.95 | 2.68 | 3.663(1) | 125.53 |
| C(12)-H(12)...O(6)#4 | 0.95 | 2.60 | 3.398(6) | 141.2 |

2.2H₂O

| C(2)-H(2)...O(3)#2 | 0.95 | 2.41 | 3.328(6) | 163.1 |
| C(4)-H(4)...O(3)#3 | 0.95 | 2.66 | 3.344(6) | 129.0 |

3.2H₂O

| C(2)-H(2)...O(4)#1 | 0.95 | 2.40 | 3.323(6) | 163.1 |
| C(4)-H(4)...O(3)#2 | 0.95 | 2.60 | 3.238(7) | 124.9 |

4-Heating

| C(13)-H(13)...O(3)#2 | 0.95 | 2.36 | 3.121(5) | 137.3 |
| C(14)-H(14)...O(6)#2 | 0.95 | 2.43 | 3.316(4) | 154.4 |
| C(4)-H(4)...O(6)#3 | 0.95 | 2.68 | 3.357(5) | 129.0 |

4-Vapour diffusion

| C(13)-H(13)...O(3)#2 | 0.95 | 2.36 | 3.122(5) | 137.1 |
| C(14)-H(14)...O(6)#2 | 0.95 | 2.42 | 3.308(6) | 155.0 |
| C(4)-H(4)...O(6)#3 | 0.95 | 2.66 | 3.345(5) | 129.3 |

| C(6)-H(6A)...O(6)#3 | 0.99 | 2.54 | 3.366(5) | 140.4 |

Symmetry transformations used to generate equivalent atoms:

For 1: #1 -x+1,-y+1,-z  #2 -x+1,-y,-z+1  #3 -x,-y+2,-z  #4 -x+1,-y+1,-z+1
For 1-2H₂O: #2 -x+1,-y+1,-z  #3 x,+y+1,+z  #4 -x+1,-y+1,-z+1
For 1 (Regenerated): #1 x,y,z, #2 x-1,y,z, #3 –x, -y+1, -z, #4 x,y+1,z,
For 2: #1 x-1,y,z  #2 x+1,y,z  #3 -x,-y+1,-z  #4 x,y+1,z,
For 2-2H₂O: #1 x-1,y,z
For 2 (Regenerated): #1 x-1,y,z  #2 -x+1,-y+1,-z+1  #3 -x,-y+2,-z+1  #4 -x+1,-y+1,-z+1
For 3: #1 x-1,y,z  #2 -x+1,-y+1,-z+1  #3 x,y-1,-z  #4 -x+1,-y,-z+1
For 4-Heating: #1 -x+2,-y,-z  #2 -x+2,-y+2,-z+2  #3 -x+1,-y,-z+1
For 4-Vapour diffusion: #1 -x+1,-y,-z+1  #2 -x+1,-y+1,-z+2  #3 -x+1,-y+1,-z+1
Fig. S1 Showing water tetramers along the $\alpha$-axis: (a) for 1.2H$_2$O (b) for 2.2H$_2$O and (c) for 3.2H$_2$O.
Fig. S2 Hydrogen bonded 2D polymeric chain along the $a$-axis: (a) for $\text{1.2H}_2\text{O}$ (b) for $\text{2.2H}_2\text{O}$ and (c) for $\text{3.2H}_2\text{O}$.

Packing diagrams of $\text{1.2H}_2\text{O}-\text{3.2H}_2\text{O}$ also reveal the presence of two types of hydrogen bonding: (i) one of the hydrogen atoms of each water molecule in the water tetramer is linked with one of the oxygen atoms of the bidentate OR or OR' group through O-H····O hydrogen bonding and (ii) C-H····O interaction between the pyridine C-H of hep$^-$ and the oxygen atom of the bidentate OR or OR' group leading to the formation of a hydrogen bonded 2D polymeric chain. Moreover, $\text{2.2H}_2\text{O}$ and $\text{3.2H}_2\text{O}$ also exhibit strong π····π stacking interactions between the two pyridine rings of two bridging hep$^-$ ligands associated with the two adjacent dimeric units, with centroid to centroid distances of 3.377 and 3.358 Å, respectively, thus, further stabilizing the 2D polymeric chains.
Fig. S3 Hydrogen bonded 1D polymeric chain along the $a$-axis: (a) 1 and (b) 2.

The packing diagrams of 1 and 2 establish the presence of C-H···O hydrogen bonding between the pyridine C-H of hepa and the axial oxygen atoms O3 from two different dimeric molecules. Moreover, in 2 the π · · π stacking interactions between the pyridine rings of hepa of two neighboring dimeric units, with centroid to centroid distance of 3.612 Å, yields a 1D polymeric chain. If the weak interactions are ignored then $1.2H_2O \rightarrow 1$ and $2.2H_2O \rightarrow 2$ can be considered as 1D to 0D transformations.
**Fig. S4** (a) In 4 each tetramer is hydrogen bonded with six surrounding tetramers and (b) Hydrogen bonded 3D polymeric chain of 4 along the $a$-axis.

The packing diagram of 4 reveals the presence of intermolecular C-H· · ·O hydrogen bonding between the hydrogen atoms H(4), H(13), H(14) of the pyridine ring of hep$^-$ ligand and the apical oxygen atom O(3) of the chelated O$^6$Pr$^-$ ligand/pendant oxygen atom O(6) of $\mu$-O$^6$Pr$^-$. Thus, each tetramer is surrounded by six neighboring tetramers yielding a 3D polymeric chain.
**Fig. S5** IR spectra of (a) 1.2H₂O (Blue crystal), (b) 1 (Blue crystal) and (c) 1.2H₂O - Regenerated (Blue crystal) in KBr disk.
Fig. S6 IR spectra of (a) $2\text{H}_2\text{O}$ (Blue crystal), (b) 2 (Blue crystal) and (c) $2\text{H}_2\text{O}$ - Regenerated (Blue crystal) in KBr disk.
Fig. S7 IR spectra of (a) 3.2H₂O (Blue crystal), (b) 4-Heating (Green crystal) and (c) 4- Vapour (Green crystal) in KBr disk.
**Fig. S8** TGA of (a) 1.2H₂O (Blue crystal), (b) 1 (Blue crystal) and (c) 1.2H₂O-Regenerated (Blue crystal).
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<th>Compound No.</th>
<th>Temperature (°C) Range</th>
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<tr>
<td>(b)</td>
<td>2</td>
<td>Upto 200</td>
<td>No weight Loss</td>
</tr>
<tr>
<td>(c)</td>
<td>1.2H₂O(Regenerated)</td>
<td>110.34</td>
<td>94.147</td>
</tr>
</tbody>
</table>

**Fig. S9**  TGA of (a) 2.2H₂O (Blue crystal), (b) 2 (Blue crystal) and (c) 2.2H₂O-Regenerated (Blue crystal).
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Compound No.</th>
<th>Temperature (°C) Range</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>3.2H₂O</td>
<td>96.59</td>
<td>92.569</td>
</tr>
<tr>
<td>(b)</td>
<td>4</td>
<td>Upto 180</td>
<td>No weight Loss</td>
</tr>
</tbody>
</table>

**Fig. S10** TGA of (a) 3.2H₂O (Blue crystal) and (b) 4 (Green crystal).
Fig. S11 Powder XRD patterns for 4 by vapor diffusion in different solvent vapor a) MeOH b) EtOH c) 'PrOH and d) ACN.