Electronic Supplementary Material (ESI) for Dalton Transactions


# Supporting Information

# Syntheses, structures and physical properties of transition metal-organic frameworks assembled from trigonal heterofunctional ligand

Shu-Yan Song,[a] Xue-Zhi Song,[a,b] Shu-Na Zhao,[a,b] Chao Qin,[a] Sheng-Qun Su,[a,b] Min Zhu,[a,b] Zhao-Min Hao,[a,b] Hong-Jie Zhang*[,a]

[a]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China
[b]Graduate School of the Chinese Academy of Sciences, Beijing, 100039, China

*Corresponding author

Email: hongjie@ciac.jl.cn (Hong-Jie Zhang)

Tel: 86-431-85262127.

Fax: 86-431-85698041.

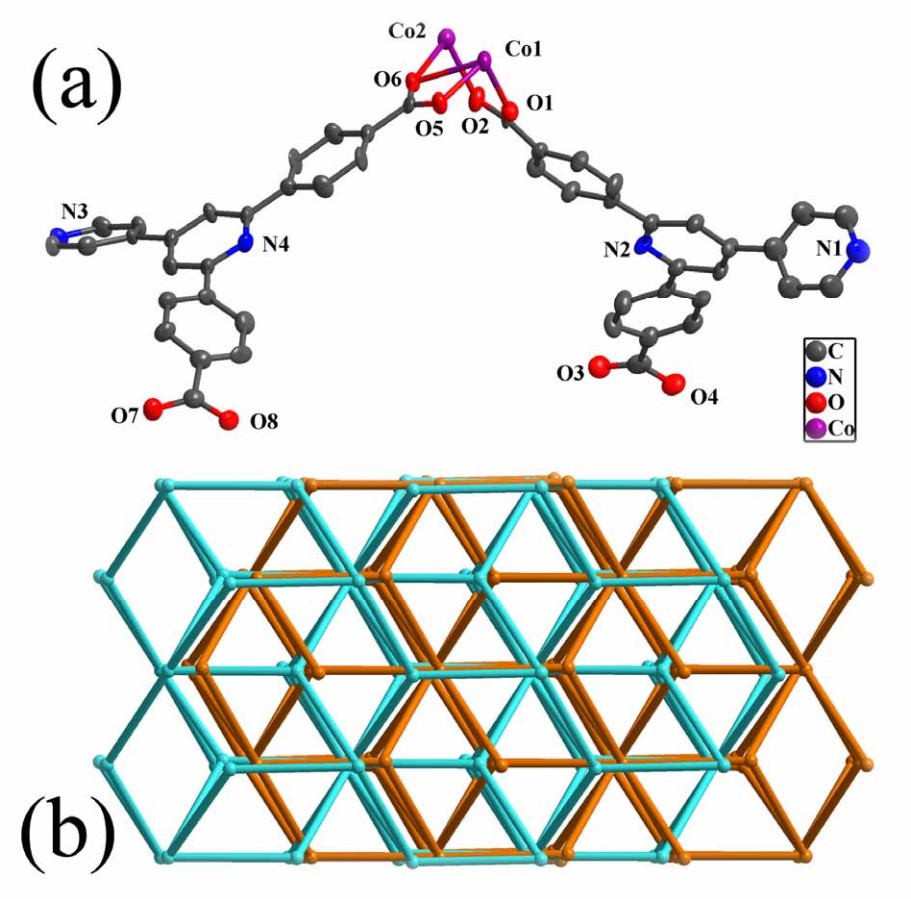



**Fig. S1** Supplementary structural description of **2**. (a) ORTEP drawing of asymmetric unit in **2** (50% probability ellipsoids). Hydrogen atoms and lattice water molecule are omitted for clarity. (b) Schematic representation of the 2-fold interpenetrating frameworks.

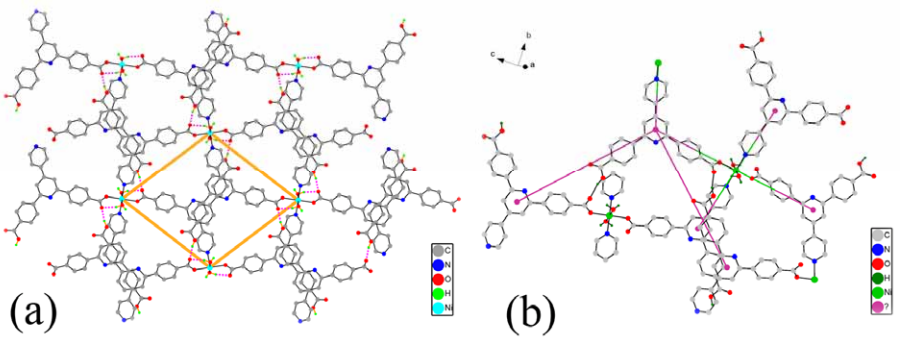
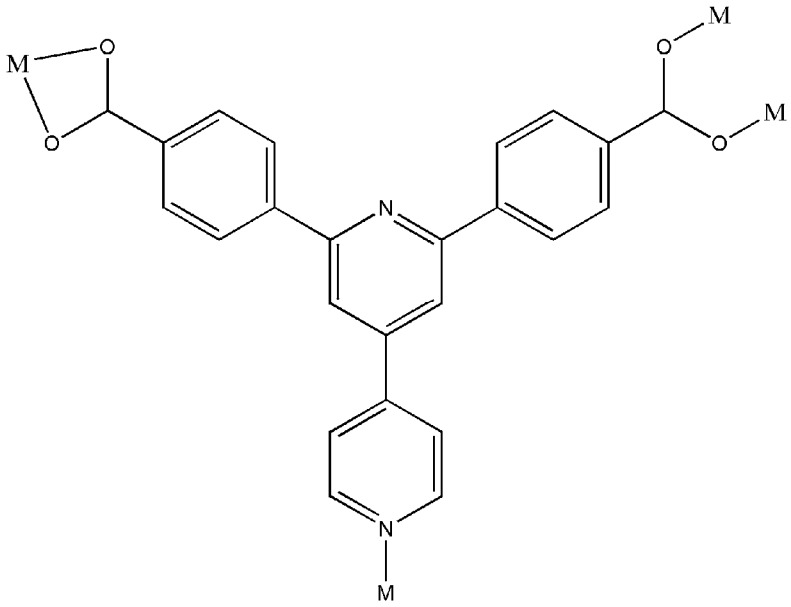



**Fig. S2** Supplementary structural description of **3**. (a) Schematic view of the single layer in **3**, pink dash lines represent hydrogen bonds and yellow rods represent that nickel ions are ligated by linear linker. (b) Schematic diagram of two kinds of 4-connected nodes and their connectivity. In this structure, the violet and green spheres represent independent $bpydbH^{1-}$ ligands and the Ni(II) ions, respectively.

**Text S1**: Detail description of the structures of **4**.

Although, compound **4** crystallizes in the same space group as compound **2**, herein some points different from **2** will be presented. Comparing with the $Co^{2+}$ ions, the ions radius of $Cu^{2+}$ is shorter than $Co^{2+}$ which means that $Cu^{2+}$ may adopt a lower coordination number of five. Cu1 is coordinated by O4, O6A, O7C, O8C and N3D; Cu2 is coordinated by O1, O2, O3, O5A and N1B. Both Cu1 and Cu2 display distorted tetragonal pyramid coordination geometries, which can be indicated by the calculated value of the $\tau_5$ parameter ($\tau_5 \approx 0.057$, 0.032 for Cu1 and Cu2, respectively) introduced by introduced by Addison, Reedijk and coworkers in 1984.[S1] The axial positions of tetragonal pyramid geometries around Cu1 and Cu2 were occupied by O8C and O2, respectively. One of the two carboxylate groups in $\mu_2$-$\eta^1$:$\eta^1$ fashion with syn-syn conformation bridges Cu1 and Cu2 to form a bimetallic secondary building unit (SBU) with the Cu1⋯Cu2 separation of 2.884 Å.

**Reference S1**: A.W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.




**Scheme S1**: Schematic diagram of the existing form and coordination mode of the ligand bpydb$H_2$ in **4**.

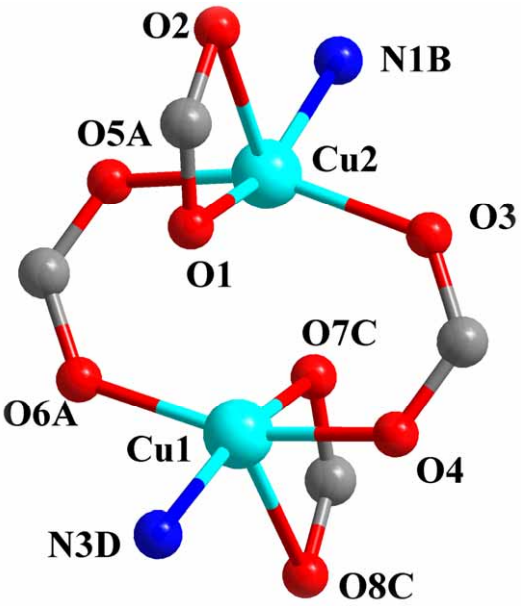



**Fig. S3** Schematic view of coordination environment of Cu(II) ions in **4**. Symmetry codes: A = x,-y,-1/2+z; B = -1/2+x,1/2-y,-1/2+z; C = x,2-y,-1/2+z; D = 1/2+x,-1/2+y,z.

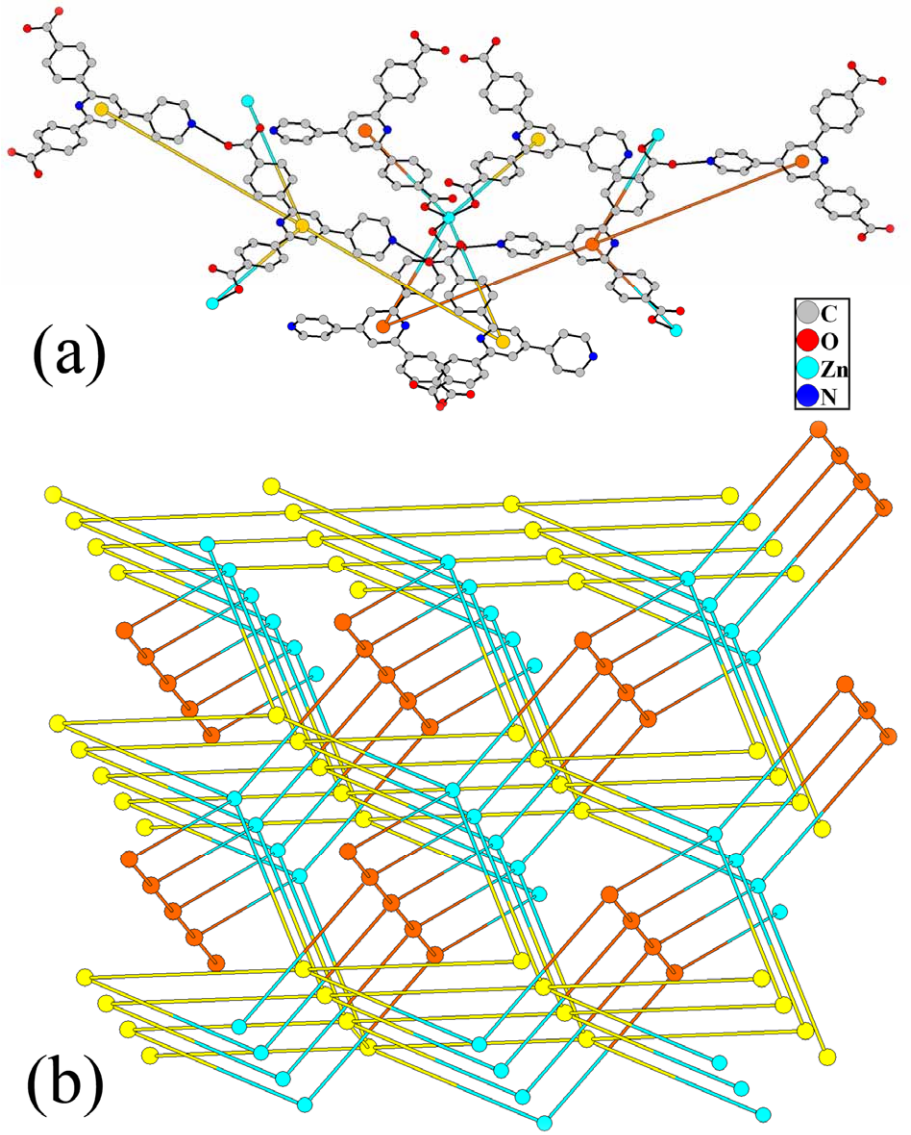



**Fig. S4** (a) Schematic diagram of the nodes and their connectivity. (b) Schematic view of the 4-connected single framework in **5**. In this framework, the yellow and orange spheres represent two independent $bpyHdb^{1-}$ ligands, and the cyan spheres represent the Zn(II) ions.

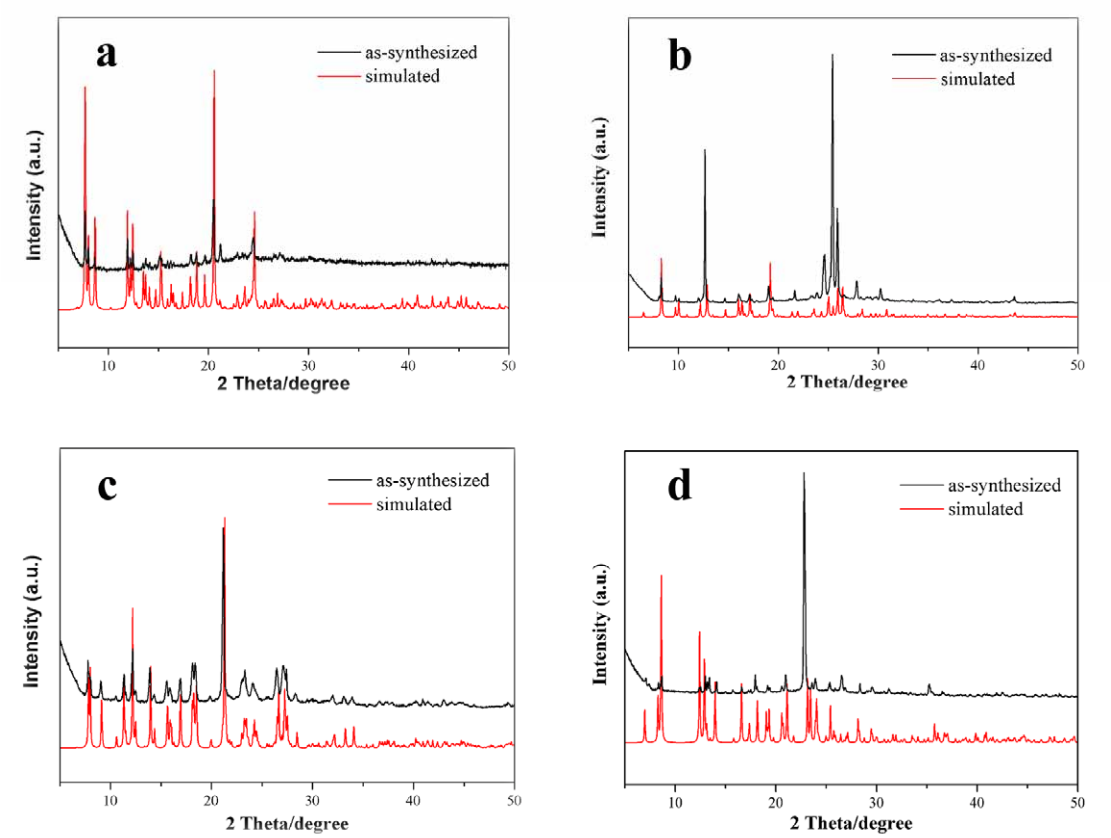



**Fig. S5** Simulated (red) and experimental as-synthesized (black) powder X-ray diffraction (PXRD) patterns of **2**(a), **3**(b), **5**(c) and **6**(d).

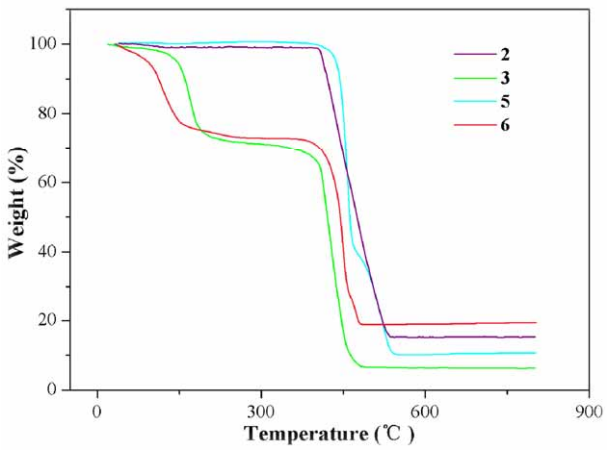



**Fig. S6** TGA curve of compounds **2**, **3**, **5** and **6**.

**Table S1**: Selected bond lengths (Å) and angles (deg) for complexes **1-6**.

| | | | |
|---|---|---|---|
| | | Complex **1** | |
| Mn1-O1 | 2.187(3) | Mn1-O7#4 | 2.110(3) |
| Mn1-O2 | 2.403(3) | Mn1-O6#5 | 2.122(3) |
| Mn1-O3 | 2.225(3) | Mn1-N1#6 | 2.244(3) |
| O7#4-Mn1-O6#5 | 89.86(13) | O7#4-Mn1-O1 | 93.50(13) |
| O6#5-Mn1-O1 | 104.93(13) | O7#4-Mn1-O3 | 171.33(11) |
| O6#5-Mn1-O3 | 91.84(13) | O1-Mn1-O3 | 94.27(12) |
| O7#4-Mn1-N1#6 | 92.44(12) | O6#5-Mn1-N1#6 | 106.33(14) |
| O1-Mn1-N1#6 | 148.17(12) | O3-Mn1-N1#6 | 78.92(12) |
| O7#4-Mn1-O2 | 95.33(12) | O6#5-Mn1-O2 | 160.85(13) |
| O1-Mn1-O2 | 56.43(10) | O3-Mn1-O2 | 85.79(12) |
| N1#6-Mn1-O2 | 91.88(11) | | |
| | | Complex **2** | |
| Co1-O1 | 2.030(5) | Co1-O5 | 2.041(5) |
| Co1-O6 | 2.381(5) | Co1-O8#5 | 2.011(6) |
| Co1-N3#6 | 2.068(6) | Co1-O4#7 | 2.273(6) |
| Co2-O6 | 2.267(6) | Co2-O7#5 | 2.056(6) |
| Co2-N1#8 | 2.082(8) | Co2-O3#7 | 2.088(6) |
| Co2-O4#7 | 2.258(6) | Co2-C19#7 | 2.474(8) |
| O8#5-Co1-O1 | 162.2(2) | O8#5-Co1-O5 | 93.1(2) |
| O1-Co1-O5 | 94.6(2) | O8#5-Co1-N3#6 | 100.5(2) |
| O1-Co1-N3#6 | 91.7(2) | O5-Co1-N3#6 | 111.0(2) |
| O8#5-Co1-O4#7 | 86.6(2) | O1-Co1-O4#7 | 80.6(2) |
| O5-Co1-O4#7 | 159.4(2) | N3#6-Co1-O4#7 | 89.2(2) |
| O8#5-Co1-O6 | 86.2(2) | O1-Co1-O6 | 84.0(2) |
| O5-Co1-O6 | 59.1(2) | N3#6-Co1-O6 | 168.7(2) |
| O4#7-Co1-O6 | 100.4(2) | O7#5-Co2-O2 | 161.4(2) |
| O7#5-Co2-N1#8 | 96.0(3) | O2-Co2-N1#8 | 97.1(3) |
| O7#5-Co2-O3#7 | 93.1(2) | O2-Co2-O3#7 | 97.5(3) |
| N1#8-Co2-O3#7 | 100.2(3) | O7#5-Co2-O4#7 | 83.4(2) |
| O2-Co2-O4#7 | 88.4(2) | N1#8-Co2-O4#7 | 161.2(3) |
| O3#7-Co2-O4#7 | 61.2(2) | O7#5-Co2-O6 | 81.1(2) |
| O2-Co2-O6 | 84.9(2) | N1#8-Co2-O6 | 94.0(3) |
| O3#7-Co2-O6 | 165.2(2) | O4#7-Co2-O6 | 104.4(2) |
| | | Complex **3** | |
| Ni1-O1#2 | 2.0548(19) | Ni1-O1#3 | 2.0548(19) |
| Ni1-O1w | 2.086(2) | Ni1-O1w#4 | 2.086(2) |
| Ni1- N2 | 2.094(2) | Ni1-N2#4 | 2.094(2) |
| O1#2-Ni1-O1#3 | 180.0 | O1#2-Ni1-O1w#4 | 88.19(9) |
| O1#3-Ni1-O1w#4 | 91.81(9) | O1#2-Ni1-O1w | 91.81(9) |
| O1#3-Ni1-O1w | 88.19(9) | O1w#4-Ni1-O1w | 180.00(11) |
| O1#2-Ni1-N2 | 89.12(8) | O1#3-Ni1-N2 | 90.88(8) |
| O1w#4-Ni1-N2 | 91.97(9) | O1w-Ni1-N2 | 88.03(9) |

| | | | |
|---|---|---|---|
| O1#2-Ni1-N2#4 | 90.88(8) | O1#3-Ni1-N2#4 | 89.12(8) |
| O1w#4-Ni1-N2#4 | 88.03(9) | O1w-Ni1-N2#4 | 91.97(9) |
| N2-Ni1-N2#4 | 180.0 | | |
| | | Complex **4** | |
| Cu1-O4 | 1.935(4) | Cu1-N3#6 | 1.993(5) |
| Cu1-O6#5 | 1.936(4) | Cu1-O7#7 | 2.019(4) |
| Cu1-O8#7 | 2.336(5) | Cu2-O1 | 1.976(4) |
| Cu2-O2 | 2.352(5) | Cu2-O3 | 2.000(4) |
| Cu2-N1#8 | 1.969(7) | Cu2-O5#5 | 1.975(4) |
| O4-Cu1-O6#5 | 160.1(2) | O4-Cu1-N3#6 | 94.1(2) |
| O6#5-Cu1-N3#6 | 89.00(19) | O4-Cu1-O7#7 | 91.46(18) |
| O6#5-Cu1-O7#7 | 91.02(18) | N3#6-Cu1-O7#7 | 163.5(2) |
| O4-Cu1-O8#7 | 91.51(19) | O6#5-Cu1-O8#7 | 106.73(19) |
| N3#6-Cu1-O8#7 | 104.7(2) | O7#7-Cu1-O8#7 | 59.63(17) |
| N1#8-Cu2-O5#5 | 92.8(3) | N1#8-Cu2-O1 | 157.5(2) |
| O5#5-Cu2-O1 | 92.39(19) | N1#8-Cu2-O3 | 93.7(3) |
| O5#5-Cu2-O3 | 155.57(19) | O1-Cu2-O3 | 90.58(19) |
| N1#8-Cu2-O2 | 97.3(2) | O5#5-Cu2-O2 | 99.81(19) |
| O1-Cu2-O2 | 60.27(18) | O3-Cu2-O2 | 102.70(19) |
| | | Complex **5** | |
| Zn1-O1 | 2.019(2) | Zn1-O5 | 1.990(2) |
| Zn1-O3#3 | 1.958(3) | Zn1-O8#4 | 1.984(3) |
| O3#3-Zn1-O8#4 | 131.75(11) | O3#3-Zn1-O5 | 109.28(11) |
| O8#4-Zn1-O5 | 100.54(11) | O3#3-Zn1-O1 | 103.04(10) |
| O8#4-Zn1-O1 | 109.27(11) | O5-Zn1-O1 | 98.28(10) |
| | | Complex **6** | |
| Cd1-O1 | 2.295(3) | Cd1-O1#4 | 2.295(3) |
| Cd1-O3 | 2.417(3) | Cd1-O3#4 | 2.417(3) |
| Cd1-O2 | 2.474(3) | Cd1-O2#4 | 2.474(3) |
| Cd1-N1#3 | 2.293(4) | | |
| N1#3-Cd1-O1 | 136.02(7) | N1#3-Cd1-O1#4 | 136.02(7) |
| O1-Cd1-O3#4 | 108.04(12) | O1#4-Cd1-O3 | 108.04(12) |
| O1-Cd1-O3 | 82.62(12) | O1#4-Cd1-O3#4 | 82.62(12) |
| N1#3-Cd1-O3 | 82.76(8) | N1#3-Cd1-O3#4 | 82.76(8) |
| N1#3-Cd1-O2#4 | 87.69(7) | N1#3-Cd1-O2 | 87.69(7) |
| O1-Cd1-O2#4 | 130.13(11) | O1#4-Cd1-O2 | 130.13(11) |
| O3-Cd1-O2#4 | 80.84(12) | O3#4-Cd1-O2 | 80.84(12) |
| O1-Cd1-O2 | 54.10(9) | O1#4-Cd1-O2#4 | 54.10(9) |
| O3-Cd1-O2 | 98.57(13) | O3#4-Cd1-O2#4 | 98.57(13) |
| O2#4-Cd1-O2 | 175.37(14) | O3-Cd1-O3#4 | 165.53(17) |
| O1-Cd1-O1#4 | 87.95(15) | | |

Symmetry codes: Complex **1**: #4 = x+1,y,z-1; #5 = x-1,y,z-1; #6 = -x+1,y-1/2,-z+1/2; **2**: #5 = x,-y,z+1/2; #6 = x+1/2,-y+1/2,z+1/2; #7 = x,-y+2,z+1/2; #8 = x-1/2,y-1/2,z; **3**: #2 =

x-1/2,-y+3/2,z+1/2; #3 = -x+1/2,y-1/2,-z-1/2; #4 = -x,-y+1,-z; **4**: #5 = x,-y,z-1/2; #6 = x+1/2,y-1/2,z; #7 = x,-y+2,z-1/2; #8 = x-1/2,-y+1/2,z-1/2; **5**: #3 = x-1,y-1,z; #4 = x+1,y-1,z; **6**: #3 = x-1/2,y-1/2,z-1; #4 = -x+1,y,-z+3/2.

**Table S2**: Hydrogen bonds (lengths and angles, Å and deg) for complexes **1**, **3** and **5**.

| D-H···A | *d*(D-H) | *d*(H···A) | *d*(D···A) | ∠(DHA) |
|---|---|---|---|---|
| Complex **1** | | | | |
| O(4)-H(4A)...O(5)#5 | 0.90(2) | 1.57(2) | 2.461(5) | 175(8) |
| N(3)-H(3A)...O(8)#7 | 0.92(2) | 1.90(6) | 2.555(5) | 126(6) |
| Complex **3** | | | | |
| O(1W)-H(1B)...O(5)#5 | 0.70(6) | 2.05(6) | 2.746(3) | 171(7) |
| O(1W)-H(1A)...O(2)#2 | 0.81(6) | 1.93(6) | 2.698(3) | 158(6) |
| O(3)-H(1O)...O(2)#6 | 0.894(19) | 1.74(3) | 2.595(3) | 158(5) |
| Complex **5** | | | | |
| N(2)-H(1A)...O(2)#5 | 0.902(19) | 1.94(3) | 2.669(4) | 137(4) |
| N(2)-H(1A)...O(5)#5 | 0.902(19) | 2.41(4) | 3.083(4) | 132(4) |
| N(4)-H(2A)...O(6)#6 | 0.899(19) | 1.95(3) | 2.721(4) | 142(4) |
| N(4)-H(2A)...O(1)#6 | 0.899(19) | 2.49(4) | 3.068(4) | 123(3) |
| N(4)-H(2A)...O(3)#7 | 0.899(19) | 2.58(4) | 3.028(4) | 111(3) |

Symmetry codes: Complex **1**: #5 = x-1,y,z-1; #7 = -x-1,y-1/2,-z+3/2; **3**: #2 = x-1/2,-y+3/2,z+1/2; #5 = -x+1,-y+1,-z; #6 = x-1/2,-y+5/2,z+1/2; **5**: #5 = x,y,z+1; #6 = x,y+1,z-1; #7 = x-1,y,z-1.