

Supplementary information

Table S1. Data collection and structure refinement for 1.

Theta range for data collection	1.68 to 28.29°
Index ranges	-13≤h≤13, -32≤k≤32, -13≤l≤13
Reflections collected	35905
Independent reflections	5652 [R(int) = 0.0290]
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL97 (Sheldrick, 1997)
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5652 / 0 / 309
Goodness-of-fit on F²	1.097
Final R indices	4737 data; I>2σ(I) R ₁ = 0.0306, wR ₂ = 0.0841 all data R ₁ = 0.0413, wR ₂ = 0.0966
Weighting scheme	w=1/[σ ² (F _o ²)+(0.0556P) ² +0.5697P] where P=(F _o ² +2F _c ²)/3
Largest diff. peak and hole	0.673 and -0.319 eÅ ⁻³
R.M.S. deviation from mean	0.104 eÅ ⁻³

Table S2. Data collection and structure refinement for 2.

Theta range for data collection	1.68 to 28.61°
Index ranges	-11≤h≤11, -20≤k≤21, -22≤l≤22
Reflections collected	75712
Independent reflections	11444 [R(int) = 0.0304]
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL97(Sheldrick, 1997)
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	11444 / 9 / 545
Goodness-of-fit on F²	1.051
Final R indices	8537 data; I>2σ(I) R ₁ = 0.0518, wR ₂ = 0.1488 all data R ₁ = 0.0747, wR ₂ = 0.1768
Weighting scheme	w=1/[σ ² (F _o ²)+(0.0936P) ² +2.4842P] where P=(F _o ² +2F _c ²)/3
Largest diff. peak and hole	2.042 and -1.112 eÅ ⁻³
R.M.S. deviation from mean	0.142 eÅ ⁻³

Table S3. Data collection and structure refinement for 3.

Theta range for data collection	2.47 to 25.35°
Index ranges	-10≤h≤10, -12≤k≤11, -13≤l≤13
Reflections collected	31075

Independent reflections	3217 [R(int) = 0.0244]
Max. and min. transmission	0.7680 and 0.6390
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	3217 / 4 / 204
Goodness-of-fit on F²	1.045
Final R indices	2984 data; I>2σ(I) R ₁ = 0.0343, wR ₂ = 0.0964 all data R ₁ = 0.0372, wR ₂ = 0.0999
Weighting scheme	w=1/[σ ² (F _o ²)+(0.0560P) ² +0.7835P] where P=(F _o ² +2F _c ²)/3
Largest diff. peak and hole	0.959 and -0.599 eÅ ⁻³
R.M.S. deviation from mean	0.062 eÅ ⁻³

Table S4. Data collection and structure refinement for 5.

Theta range for data collection	1.56 to 25.37°
Index ranges	-11≤h≤11, -17≤k≤17, -18≤l≤18
Reflections collected	26942
Independent reflections	6575 [R(int) = 0.0420]
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL97 (Sheldrick, 1997)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6575 / 2 / 419
Goodness-of-fit on F²	1.000
Final R indices	4821 data; I>2σ(I) R ₁ = 0.0355, wR ₂ = 0.1001 all data R ₁ = 0.0625, wR ₂ = 0.1255
Weighting scheme	w=1/[σ ² (F _o ²)+(0.0798P) ²] where P=(F _o ² +2F _c ²)/3
Largest diff. peak and hole	0.534 and -0.575 eÅ ⁻³
R.M.S. deviation from mean	0.207 eÅ ⁻³

Table S5. Data collection and structure refinement for 5.DMF.

Theta range for data collection	1.78 to 25.41°
Index ranges	-10≤h≤10, -13≤k≤13, -14≤l≤14
Reflections collected	17221
Independent reflections	3923 [R(int) = 0.0430]
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL97 (Sheldrick, 1997)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	3923 / 0 / 259
Goodness-of-fit on F²	1.146

Final R indices	3353 data; $I > 2\sigma(I)$ $R_1 = 0.0308$, $wR_2 = 0.0806$ all data $R_1 = 0.0415$, $wR_2 = 0.0966$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 0.1479P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	0.488 and -0.642 $e\text{\AA}^{-3}$
R.M.S. deviation from mean	0.181 $e\text{\AA}^{-3}$

Table S6. Data collection and structure refinement for 6.DMSO.

Theta range for data collection	1.68 to 26.38°
Index ranges	-18 ≤ h ≤ 18, -8 ≤ k ≤ 8, -26 ≤ l ≤ 26
Reflections collected	34107
Independent reflections	2467 [R(int) = 0.0880]
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2467 / 4 / 181
Goodness-of-fit on F^2	1.094
Final R indices	1631 data; $I > 2\sigma(I)$ $R_1 = 0.0484$, $wR_2 = 0.1373$ all data $R_1 = 0.0943$, $wR_2 = 0.1795$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 0.8603P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	0.630 and -0.729 $e\text{\AA}^{-3}$
R.M.S. deviation from mean	0.199 $e\text{\AA}^{-3}$

Table S7. Coordination environment bond angles around the metal atoms (°)

1	O1-Zn1-N3	96.97(7)	O1-Zn1-N4	98.21(6)
	N3-Zn1-N4	72.21(6)	O1-Zn1-S2	103.60(5)
	N3-Zn1-S2	149.15(4)	N4-Zn1-S2	82.20(4)
	O1-Zn1-S1	108.25(5)	N3-Zn1-S1	81.33(4)
	N4-Zn1-S1	144.53(4)	S2-Zn1-S1	112.849(19)
2	O1-Zn1-N4	97.14(12)	O1-Zn1-N3	98.24(12)
	N4-Zn1-N3	73.46(10)	O1-Zn1-S2	106.78(10)
	N4-Zn1-S2	82.46(8)	N3-Zn1-S2	147.15(8)
	O1-Zn1-S1	99.40(9)	N4-Zn1-S1	150.87(8)
	N3-Zn1-S1	80.53(7)	S2-Zn1-S1	115.01(4)
	O2-Zn2-N9	98.86(12)	O2-Zn2-N10	99.58(11)
	N9-Zn2-N10	73.08(10)	O2-Zn2-S3	106.35(9)
	N9-Zn2-S3	82.29(8)	N10-Zn2-S3	146.59(8)
	O2-Zn2-S4	100.03(9)	N9-Zn2-S4	149.71(8)

	N10-Zn2-S4	80.58(7)	S3-Zn2-S4	114.39(4)
3	N3-Zn1-N4	74.46(9)	N3-Zn1-S1	80.37(6)
	N4-Zn1-S1	141.87(7)	N3-Zn1-S2	151.07(7)
	N4-Zn1-S2	79.59(7)	S1-Zn1-S2	114.42(3)
	N3-Zn1-S2	102.10(7)	N4-Zn1-S2	101.94(7)
	S1-Zn1-S2	111.12(3)	S2-Zn1-S2	95.51(2)
5	N3-Cu1-N4	79.80(12)	N3-Cu1-S2	164.87(9)
	N4-Cu1-S2	85.08(9)	N3-Cu1-S1	85.10(9)
	N4-Cu1-S1	164.42(9)	S2-Cu1-S1	109.95(4)
	N9-Cu2-N10	80.51(12)	N9-Cu2-S3	85.54(9)
	N10-Cu2-S3	166.02(9)	N9-Cu2-S4	165.22(9)
	N10-Cu2-S4	85.03(9)	S3-Cu2-S4	108.94(4)
5.DMF	N4-Cu1-N3	80.81(9)	N4-Cu1-S2	85.59(6)
	N3-Cu1-S2	166.40(6)	N4-Cu1-S1	165.09(6)
	N3-Cu1-S1	85.26(6)	S2-Cu1-S1	108.27(3)
6.DMSO	N3-Ni1-N4	83.5(2)	N3-Ni1-S1	86.9(2)
	N4-Ni1-S1	170.4(2)	N3-Ni1-S2	171.3(2)
	N4-Ni1-S2	87.8(2)	S1-Ni1-S2	101.82(7)

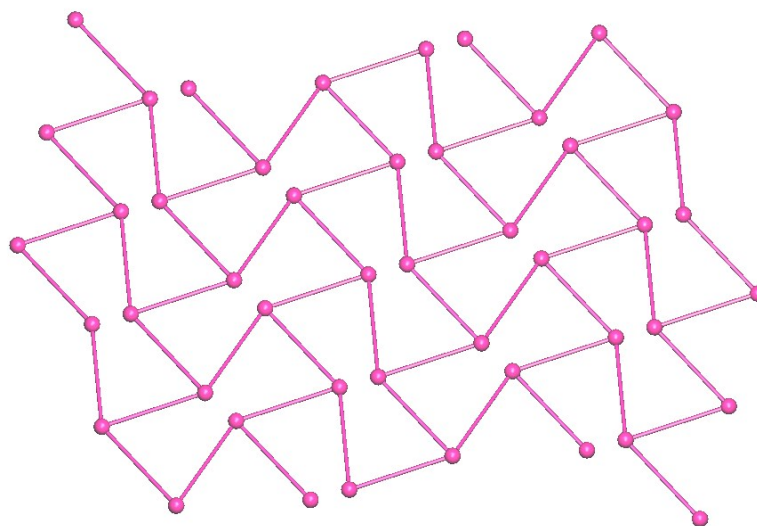


Figure S1. Perpendicular view of a layer from the triconnected uninodal underlying bidimensional **hcb** net found in compound **1**, considering the coordination compounds as nodes.