

# Exploiting dimensional variability in coordination polymers: solvent promotes reversible conversion between 3D and chiral 1D architectures

Marzio Rancan<sup>\*a,b</sup> and Lidia Armelao<sup>a,b</sup>

## Electronic Supplementary Information

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<sup>a</sup> Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131 Padova (Italy);

<sup>b</sup> IENI-CNR and INSTM, Via Marzolo 1, 35131 Padova (Italy).

E-mail: [marzio.rancan@unipd.it](mailto:marzio.rancan@unipd.it)

## Synthesis

Reagents were purchased from Aldrich and used as received.



$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (370.5 mg, 1 mmol) has been dissolved in 10 ml of DMSO in a large beaker and 4,4'-bipyridine (bpy, 302.4 mg, 2 mmol) has been added. Slow evaporation of the solvent led to deep blue single crystals suitable for X-ray analysis. If the solvent is left to completely evaporate a second kind of light blue single crystals appeared in the last evaporation stages as impurity (compound **2**, yield 1-2 % *ca.*). To avoid the impurity, single crystals of compound **1** has been removed from the solution before complete evaporation with a yield of 90 % *ca.*

Elemental analysis:

Exp: S 11.85 %, C 38.61 %, N 7.83 %, H 4.25 %

Calc: S 10.41 %, C 38.99 %, N 7.27 %, H 4.06 %

The discrepancies in elemental analysis (in particular for S) can be explained with the presence of a sixth DMSO molecule as confirmed by XRD analysis.



$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (370.5 mg, 1 mmol) has been dissolved in 10 ml of DMSO in a 20 ml vial and 4,4'-bipyridine (bpy, 302.4 mg, 2 mmol) has been added. Layering with EtOAc led to light blue single crystals after few days with a quantitative yield (98 % *ca.*). The same synthesis has been repeated in the presence of (R)-(+)-1,1'-Bi(2-naphthol) and (S)-(-)-1,1'-Bi(2-naphthol) as chiral inducing agent (abbreviations RB and SB, respectively).

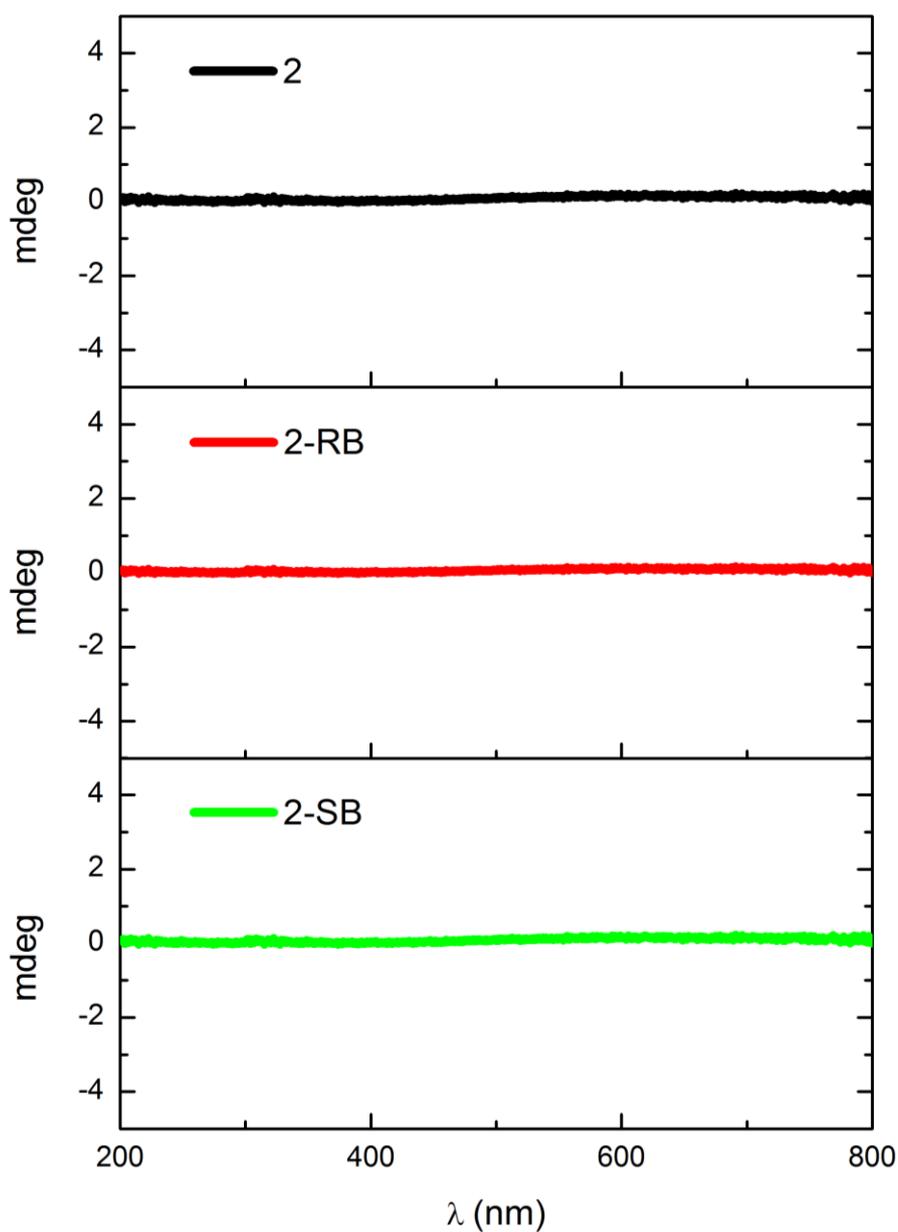
Elemental analysis:

Exp: S 17.85 %, C 30.23 %, N 2.03 %, H 4.61 %;

Calc: S 17.88 %, C 30.15 %, N 1.95 %, H 4.50%.

## Circular Dichroism (CD) spectroscopy

30 mg of compounds **2**, **2-RB** and **2-SB** have been washed with acetone, dried and ground in a mortar. A smaller portion has been put between two NaCl windows and CD spectra (Fig. S1) have been recorded with a Jasco J-715 spectropolarimeter.



**Figure S1.** CD spectra of **2**, **2-RB** and **2-SB**.

## Single crystal X-ray diffraction

Single crystals of **1** and **2** covered with Paratone-N oil were fastened on the top of a Lindemann glass capillary and centred on the head of a four-circle kappa goniometer Oxford Diffraction Gemini E diffractometer, equipped with a  $2\text{K} \times 2\text{K}$  EOS CCD area detector and sealed-tube Enhance (Mo) and (Cu) X-ray sources. Mo  $K\alpha$  ( $\lambda = 0.71070 \text{ \AA}$ ) radiation has been used for all the data collections. Data were collected at room temperature by means of the  $\omega$  - scans technique using graphite-monochromated radiation, in a  $1024 \times 1024$  pixel mode, using  $4 \times 4$  pixel binning for **1** and  $2 \times 2$  pixel binning for **2**. Detector distance was set at 90 mm for **1** and 45 mm for **2**. The diffraction intensities were corrected for Lorentz and polarization effects and were also optimized with respect to absorption. Empirical multi-scan absorption corrections using equivalent reflections were performed with the scaling algorithm SCALE3 ABSPACK. Data collection, data reduction and finalization were carried out through the CrysAlisPro software. Structures were solved by means of olex2.solve<sup>1</sup> structure solution program using Charge Flipping and refined by full-matrix least-squares methods with ShelXL<sup>2</sup> refinement package using OLEX2<sup>3</sup> software. In the last cycles of refinement, non-hydrogen atoms were refined anisotropically. Hydrogen atoms connected to carbon atoms were included in idealised positions and a riding model was used for their refinement. Crystal data and refinement parameters are reported in Table S1.

**Table S1** Crystal data and refinement parameters

<b>Compound</b>	<b>1</b>	<b>2-P3<sub>1</sub>21</b>	<b>2-P3<sub>2</sub>21</b>
Empirical formula	C <sub>50</sub> H <sub>62</sub> Cl <sub>4</sub> Cu <sub>2</sub> N <sub>8</sub> O <sub>21</sub> S <sub>5</sub>	C <sub>9</sub> H <sub>16</sub> ClCu <sub>0.5</sub> NO <sub>6</sub> S <sub>2</sub>	C <sub>9</sub> H <sub>16</sub> ClCu <sub>0.5</sub> NO <sub>6</sub> S <sub>2</sub>
Formula weight	1540.25	365.57	365.57
Temperature/K	301(2)	293(2)	293(2)
Crystal system	orthorhombic	Trigonal	trigonal
Space group	Pbca	P3 <sub>1</sub> 21	P3 <sub>2</sub> 21
a/Å	18.0973(2)	10.7197(7)	10.7314(2)
b/Å	28.4369(4)	10.7197(7)	10.7314(2)
c/Å	28.5016(3)	23.0839(12)	23.1419(6)
α/°	90	90	90
β/°	90	90	90
γ/°	90	120	120
Volume/Å <sup>3</sup>	14667.8(3)	2297.2(3)	2308.02(11)
Z	8	6	6
ρ <sub>calc</sub> /cm <sup>3</sup>	1.395	1.585	1.578
μ/mm <sup>-1</sup>	0.937	1.217	1.211
F(000)	6336.0	1131.0	1131.0
Crystal size/mm <sup>3</sup>	0.40 × 0.40 × 0.15	0.20 × 0.10 × 0.10	0.35 × 0.10 × 0.10
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.502 to 56.462	4.73 to 58.546	4.382 to 58.474
Reflections collected	16901	10332	10534
Independent reflections	16901	3634	3609
Data/restraints/parameters	16901/823/900	3634/0/181	3609/0/181
Goodness-of-fit on F <sup>2</sup>	1.029	1.061	1.078
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.1141, wR <sub>2</sub> = 0.3251	R <sub>1</sub> = 0.0328, wR <sub>2</sub> = 0.0845	R <sub>1</sub> = 0.0334, wR <sub>2</sub> = 0.0826
Final R indexes [all data]	R <sub>1</sub> = 0.1406, wR <sub>2</sub> = 0.3447	R <sub>1</sub> = 0.0382, wR <sub>2</sub> = 0.0877	R <sub>1</sub> = 0.0380, wR <sub>2</sub> = 0.0854
Largest diff. peak/hole / e Å <sup>-3</sup>	2.58/-1.09	0.55/-0.38	0.57/-0.44
Flack parameter	---	0.004(6)	0.009(6)
CCDC number	1402764	1402765	1402766

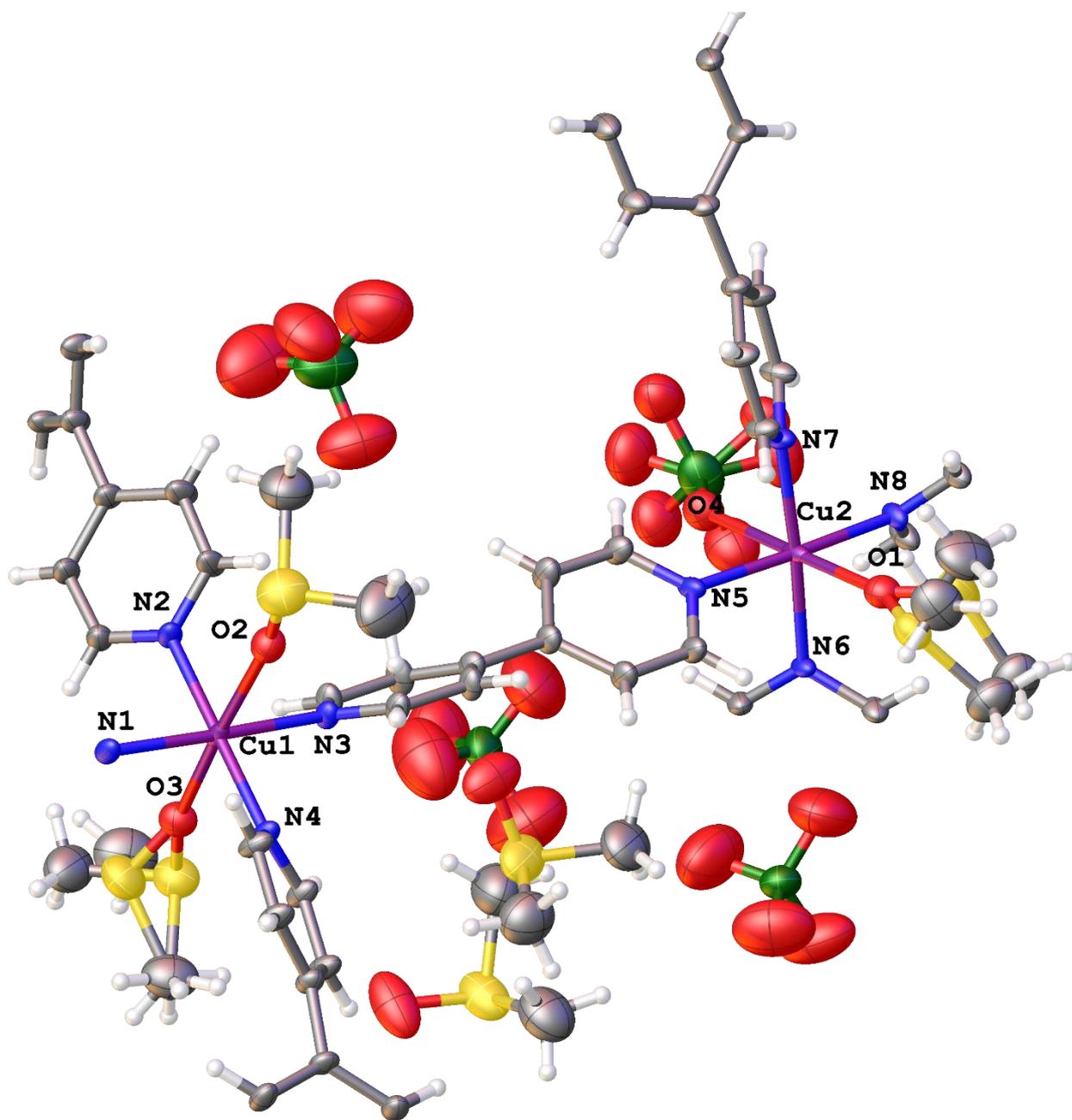
$R_1 = (\sum ||F_o| - |F_c|| / \sum |F_o|)$ ;  $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ ;  $GOF = \sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$  where  $n$  is the number of data and  $p$  is the number of parameters refined.

## Data collection and refinement details for 1

Several crystals were measured with the detector at a standard distance (45 mm). We tried to solve the structure first with a tetragonal space group and after with an orthorhombic one, but in each case we did not succeed. A frames inspection revealed the presence of overlapped diffraction spots. We suspected that this could be a consequence of the quite long unit cell axes ( $a$  and  $b$  are 28 Å *ca.*), hence we set the detector at 90 mm. In this case, frames inspection revealed a lower degree of overlapping. CrysAlisPro software suggested a tetragonal space group, but the structure could not be solved (neither by direct method, Patterson or charge flipping). On the contrary, the structure could be easily solved in the  $Pbca$  orthorhombic space group. During the refinement, some atoms (O5, O6, O7, S2, S3, C43) have been splitted in two parts the occupancies of which were constrained to sum to 1.0. Restraints such as DFIX and SADI have been used to better model  $\text{ClO}_4^-$  anions and bonds where splitted atoms are involved (see below). RIGU has been applied to the whole structure. The final difference Fourier map revealed the presence of non-negligible residual peaks. They could likely be assigned to a DMSO molecule but they could not be effectively modelled. The contribution of these peaks was removed using the mask routine of OLEX2. The program calculated a total solvent accessible volume/cell of 1786.3 Å<sup>3</sup> (12 %), and a total electron-count/cell of 392 electrons. Such value closely fit the presence of 8 DMSO molecules in the unit cell ( $Z = 8$ ). This confirms the presence of a six DMSO molecules in the asymmetric unit (see elemental analysis). Two residual density peaks of 1.95 and 2.58 e/Å<sup>3</sup> are still present close to Cu1 and Cu2, respectively.

### DFIX and SADI restraints:

```
DFIX 2.25 0.01 O18 O20 O18 O21 O18 O19 O20 O21 O20 O19 O21 O19
DFIX 2.25 0.01 O4 O5 O4 O6 O4 O7 O5 O6 O5 O7 O6 O7
DFIX 2.25 0.01 O4 O5A O4 O6A O4 O7A O5A O6A O5A O7A O6A O7A
SADI S2A O3 S2B O3
SADI S3B O1 S3B O1
SADI 0.01 C12 O20 C12 O19 C12 O18 C12 O21
SADI C11 O4 C11 O5 C11 O7A C11 O7 C11 O6A C11 O6 C11 O5A
SADI C14 O10 C14 O11 C14 O12 C14 O13
SADI 0.005 O11 O12 O11 O10 O13 O12 O13 O12 O10 O13
SADI S3B C41B S3B C40B S3A C41A S3A C40A
SADI S2B C43B S2A C43A
SADI S2A C43A S2B C43B S2B C42 S2A C42
```



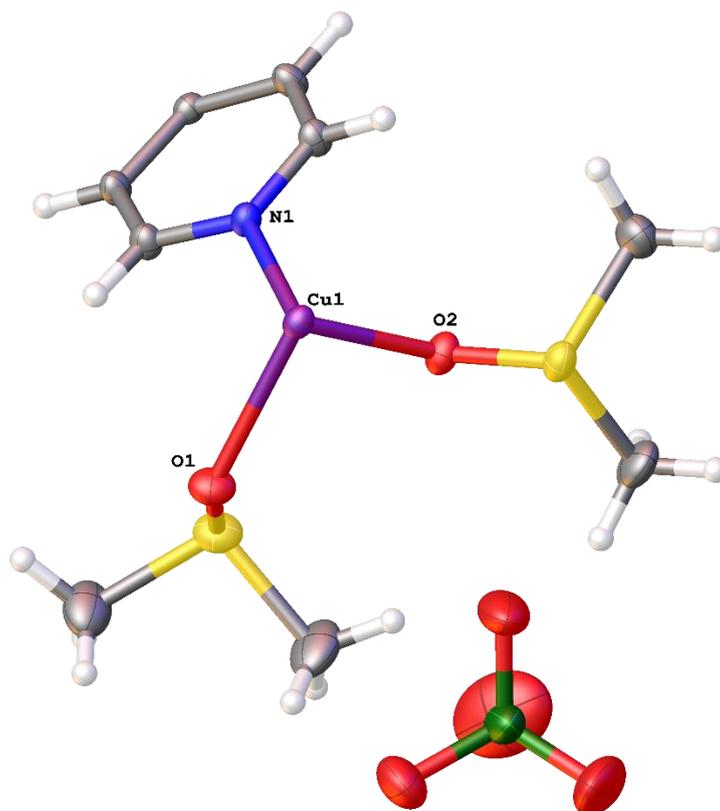
**Figure S2.** Asymmetric unit of **1**, thermal ellipsoids drawn at the 50% probability level. Colour code: Cu purple, Cl green, S yellow, O red, N blue, C grey, H white.

*Data collection and refinement details for 2*

Several crystals were measured with the detector at a standard distance (45 mm) and their absolute configuration determined.

**Table S2** Flack parameter and space group for eight randomly selected crystals of **2**

Flack parameter	Space Group
0.009(6)	P <sub>3</sub> <sub>2</sub> 21
0.004(6)	P <sub>3</sub> <sub>1</sub> 21
0.007(5)	P <sub>3</sub> <sub>1</sub> 21
0.003(5)	P <sub>3</sub> <sub>1</sub> 21
0.000(6)	P <sub>3</sub> <sub>2</sub> 21
0.017(7)	P <sub>3</sub> <sub>2</sub> 21
0.005(8)	P <sub>3</sub> <sub>1</sub> 21
-0.001(6)	P <sub>3</sub> <sub>2</sub> 21



**Figure S3** Asymmetric unit of **2-P<sub>3</sub><sub>2</sub>21**, thermal ellipsoids drawn at the 50% probability level. Colour code: Cu purple, Cl green, S yellow, O red, N blue, C grey, H white.

**Table S3** Selected bond lengths for **2-P3<sub>1</sub>21** and **2-P3<sub>2</sub>21**

<b>2-P3<sub>1</sub>21</b>			<b>2-P3<sub>2</sub>21</b>		
<b>Atom</b>	<b>Atom</b>	<b>Length/Å</b>	<b>Atom</b>	<b>Atom</b>	<b>Length/Å</b>
Cu1	O2	2.012(2)	Cu1	O2	2.015(2)
Cu1	N1	2.018(2)	Cu1	N1	2.022(2)
Cu1	O1	2.329(3)	Cu1	O1	2.330(3)

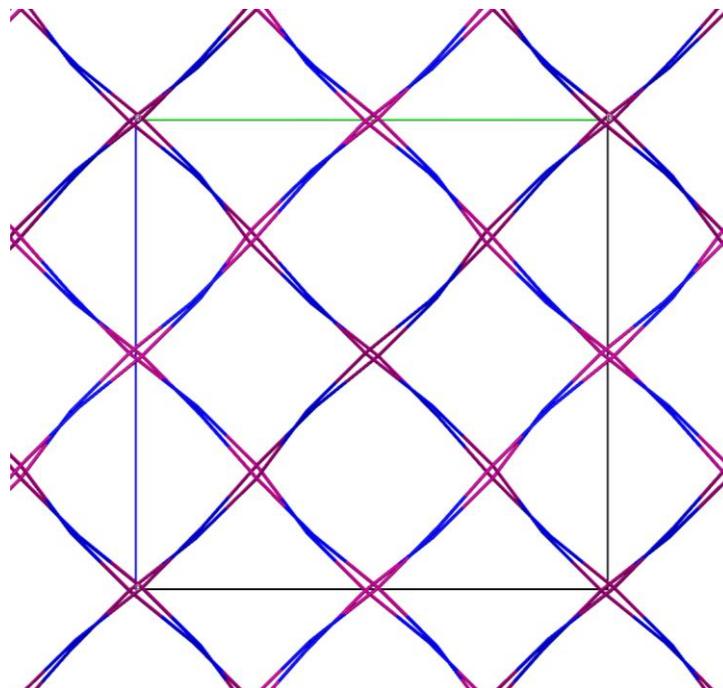
**Table S4** Selected angles for **2-P3<sub>1</sub>21** and **2-P3<sub>2</sub>21**

<b>2-P3<sub>1</sub>21</b>				<b>2-P3<sub>1</sub>21</b>			
<b>Atom</b>	<b>Atom</b>	<b>Atom</b>	<b>Angle/°</b>	<b>Atom</b>	<b>Atom</b>	<b>Atom</b>	<b>Angle/°</b>
O2 <sup>1</sup>	Cu1	O2	94.50(15)	O2 <sup>1</sup>	Cu1	O2	94.44(15)
O2 <sup>1</sup>	Cu1	N1	178.21(12)	O2	Cu1	N1	87.20(10)
O2 <sup>1</sup>	Cu1	N1 <sup>1</sup>	87.20(10)	O2 <sup>1</sup>	Cu1	N1	178.30(12)
O2	Cu1	N1	87.20(10)	O2	Cu1	N1 <sup>1</sup>	178.30(12)
O2	Cu1	N1 <sup>1</sup>	178.21(12)	O2 <sup>1</sup>	Cu1	N1 <sup>1</sup>	87.20(10)
O2	Cu1	O1	90.28(10)	O2	Cu1	O1 <sup>1</sup>	85.32(11)
O2	Cu1	O1 <sup>1</sup>	85.19(10)	O2 <sup>1</sup>	Cu1	O1	85.32(11)
O2 <sup>1</sup>	Cu1	O1 <sup>1</sup>	90.28(10)	O2	Cu1	O1	90.18(11)
O2 <sup>1</sup>	Cu1	O1	85.19(10)	O2 <sup>1</sup>	Cu1	O1 <sup>1</sup>	90.18(11)
N1 <sup>1</sup>	Cu1	N1	91.11(15)	N1 <sup>1</sup>	Cu1	N1	91.17(15)
N1	Cu1	O1	94.23(10)	N1	Cu1	O1	94.24(10)
N1 <sup>1</sup>	Cu1	O1 <sup>1</sup>	94.23(10)	N1 <sup>1</sup>	Cu1	O1 <sup>1</sup>	94.24(10)
N1	Cu1	O1 <sup>1</sup>	90.44(11)	N1	Cu1	O1 <sup>1</sup>	90.40(12)
N1 <sup>1</sup>	Cu1	O1	90.44(11)	N1 <sup>1</sup>	Cu1	O1	90.40(12)
O1	Cu1	O1 <sup>1</sup>	173.34(16)	O1 <sup>1</sup>	Cu1	O1	173.37(16)

<sup>1</sup> +y,+x,l-z<sup>1</sup> -y+x,-y,4/3-z

## Topological analysis of compound 1

For the purposes of analysis with TOPOS<sup>4</sup> the framework was simplified replacing the bpy ligand with its centroid as reported in Figure S4.



**Figure S4.** Square channels along the *a* axis. Colour code: Cu, purple; bpy centroid, blue.

### Topos output

```
#####  
compound 1  
#####
```

#### Topology for Cu1

-----

Atom Cu1 links by bridge ligands and has

Common vertex with				R (Å-Å)	f
Cu 2	0.7418	0.4861	0.5031 ( 0 0 0)	11.052Å	1
Cu 2	1.2582	-0.0139	0.9969 ( 2-1 1)	11.056Å	1
Cu 2	1.2418	0.0139	0.4969 ( 0 0 1)	11.057Å	1
Cu 2	0.7582	0.5139	1.0031 ( 1 1 0)	11.060Å	1

#### Topology for Cu2

-----

Atom Cu2 links by bridge ligands and has

Common vertex with				R (Å-Å)	f
Cu 1	0.9844	0.2435	0.7639 ( 0 0 0)	11.052Å	1
Cu 1	1.0156	0.7435	0.7361 ( 2 0 1)	11.056Å	1
Cu 1	0.4844	0.2565	0.2361 (-1 0 1)	11.057Å	1
Cu 1	0.5156	0.7565	0.2639 ( 1 1-1)	11.060Å	1

-----  
Structural group analysis

```

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-----
Structural group No 1
-----
Structure consists of 3D framework with CuN4C20H16
There are 2 interpenetrating nets
FISE: Full interpenetration symmetry elements
-----
1: -1
-----
PIC: [0,0,1][0,1,0][1,0,0] (PICVR=1)

Zt=1; Zn=2

Class IIa Z=2

Coordination sequences
-----
Cu1:  1  2  3  4  5  6  7  8  9  10
Num   4 10 24 44 72 104 144 188 240 296
Cum   5 15 39 83 155 259 403 591 831 1127
-----
Cu2:  1  2  3  4  5  6  7  8  9  10
Num   4 10 24 44 72 104 144 188 240 296
Cum   5 15 39 83 155 259 403 591 831 1127
-----
TD10=1127

Vertex symbols for selected sublattice
-----
Cu1 Point symbol:{4^2.8^4}
Extended point symbol:[4.4.8(4).8(4).8(8).8(8)]
-----
Cu2 Point symbol:{4^2.8^4}
Extended point symbol:[4.4.8(4).8(4).8(8).8(8)]
-----
Point symbol for net: {4^2.8^4}
4-c net; uninodal net

Topological type:  lvt,  Net  #97;  4/4/t1;  sqc176  (topos&RCSR.ttd)  {4^2.8^4}  -  VS
[4.4.8(4).8(4).8(8).8(8)] (78929 types in
2 databases)
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## References

- [1] L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Cryst.*, 2015, **A71**, 59.
- [2] G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
- [3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.
- [4] V. A. Balatov, *IUCr CompComm Newslett.*, 2006, **7**, 4.