Two Complexes of Copper(II) Salts with 5-Amino-3-(pyrid-2-yl)-*1H*-pyrazole, the Prototype for a New Class of Ditopic Ligand

Christopher M. Pask[a], Kenneth D. Camm[a], Neil J. Bullen[a], Michael J. Carr[a], William Clegg[b], Colin A. Kilner[a] and Malcolm A. Halcrow[a,*]

[a]*School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, U.K. LS2 9JT.*
Email: M.A.Halcrow@leeds.ac.uk
[b]*School of Natural Sciences, Bedson Building, University of Newcastle upon Tyne, Newcastle upon Tyne, U.K. NE1 7RU.*

Supplementary Information

Fig. S1 Views of the complex cations in the crystal structures of $[CuBrL_2]Br{\cdot}CH_3OH$ (**1**) and $[CuL_2(OH_2)]SO_4{\cdot}H_2O{\cdot}CH_3OH$ (**2**), emphasising their different molecular structures.

Table S1 Selected bond lengths and angles for $[CuBrL_2]Br{\cdot}CH_3OH$ (**1**) and $[CuL_2(OH_2)]SO_4{\cdot}H_2O{\cdot}CH_3OH$ (**2**).

Table S2 Metric parameters for the hydrogen bond and π-π interactions in $[CuBrL_2]Br{\cdot}CH_3OH$ (**1**).

Table S3 Metric parameters for the hydrogen bond and π-π interactions in $[CuL_2(OH_2)]SO_4{\cdot}H_2O{\cdot}CH_3OH$ (**2**).

Table S4 Connections making up the hydrogen-bonded network in $[CuBrL_2]Br{\cdot}CH_3OH$ (**1**).

Table S5 Connections making up the hydrogen-bonded network in $[CuL_2(OH_2)]SO_4{\cdot}H_2O{\cdot}CH_3OH$ (**2**).

Fig. S2 Two views of the topology of the extended hydrogen-bonded network in $[CuBrL_2]Br{\cdot}CH_3OH$ (**1**).

Fig. S3 Two views of the topology of the extended hydrogen-bonded network in $[CuL_2(OH_2)]SO_4{\cdot}H_2O{\cdot}CH_3OH$ (**2**).

Fig. S4 Diagram showing the relationship between the network topology for $[CuL_2(OH_2)]SO_4{\cdot}H_2O{\cdot}CH_3OH$ (**2**) and the boron nitride structure.

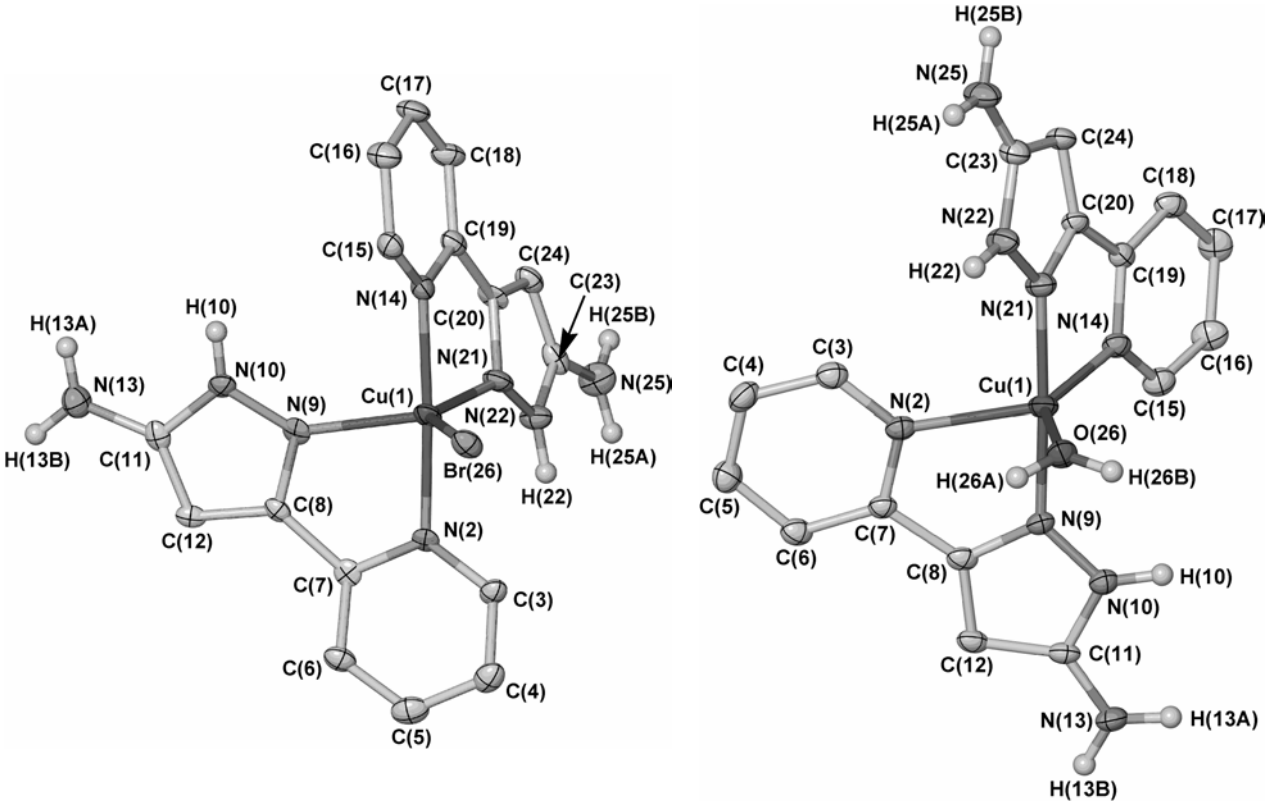

Fig. S1 Views of the complex cations in the crystal structures of $[CuBrL_2]Br{\cdot}CH_3OH$ (**1**, left) and $[Cu(OH_2)L_2]SO_4{\cdot}H_2O{\cdot}CH_3OH$ (**2**, right), emphasising their different molecular structures. All C-bound H atoms have been omitted, and displacement ellipsoids are at the 35 % probability level.

Table S1 Selected bond lengths and angles (Å, °) for $[CuBrL_2]Br{\cdot}CH_3OH$ (**1**) and $[CuL_2(OH_2)]SO_4{\cdot}H_2O{\cdot}CH_3OH$ (**2**).

T (K)	**1** (X = Br)	**2** (X = O)
Cu(1)–N(2)	1.996(8)	2.166(4)
Cu(1)–N(9)	2.089(8)	1.942(4)
Cu(1)–N(14)	1.998(8)	2.063(4)
Cu(1)–N(21)	2.035(9)	1.939(4)
Cu(1)–X(26)	2.5140(16)	2.068(3)
N(2)–Cu(1)–N(9)	80.1(3)	78.54(15)
N(2)–Cu(1)–N(14)	172.1(3)	121.22(14)
N(2)–Cu(1)–N(21)	95.0(3)	99.08(15)
N(2)–Cu(1)–X(26)	92.6(2)	100.19(13)
N(9)–Cu(1)–N(14)	95.7(3)	96.30(15)
N(9)–Cu(1)–N(21)	114.6(3)	173.76(16)
N(9)–Cu(1)–X(26)	112.8(2)	94.91(14)
N(14)–Cu(1)–N(21)	80.6(3)	79.94(16)
N(14)–Cu(1)–X(26)	95.2(2)	138.46(14)
N(21)–Cu(1)–X(26)	132.6(2)	91.18(15)

Table S2 Metric parameters for the hydrogen bond and π-π interactions in $[CuBrL_2]Br{\cdot}CH_3OH$ (**1**) (Å, °). Symmetry codes correspond to those in Fig. 1 of the main paper.

Hydrogen bonds[a]	D–H	H...A	D...A	D–H...A
N(10)–H(10)...Br(27)	0.88	2.43	3.263(8)	158.1
N(13)–H(13A)...Br(27)	0.88	2.90	3.642(9)	142.5
N(13)–H(13B)...Br(26^{i})	0.88	2.76	3.491(9)	141.6
N(22)–H(22)...O(28)	0.88	1.89	2.708(11)	154.6
N(25)–H(25A)...Br(27^{ii})	0.88	3.05	3.776(9)	141.5
N(25)–H(25B)...Br(26^{iii})	0.88	2.76	3.510(9)	143.6
O(28)–H(28)...Br(27^{iv})	0.84	2.51	3.287(8)	155.2

π-π Interactions[a]	Interplanar distance	Dihedral angle	Centroid offset
[N(2)-N(13)]-[N(2^{i})-N(13^{i})]	3.349(5)	0	2.84
[N(14)-N(25)]-[N(14^{iii})-N(25^{iii})][b]	3.59(3)	7.2(2)	2.64

[a]Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+2, y+½, -z+½$; (iii) $x+½, y, -z+½$; (iv) $-x+{}^{3}/_{2}, y+½, z$. [b]Average value quoted for distance between atoms in one ring and the plane of the other, because dihedral angle between the interacting ligands ≠ 0.

Table S3 Metric parameters for the hydrogen bond and π-π interactions in $[CuL_2(OH_2)]SO_4{\cdot}H_2O{\cdot}CH_3OH$ (**2**) (Å, °). Symmetry codes correspond to those in Fig. 2 of the main paper.

Hydrogen bonds[a]	D–H	H...A	D...A	D–H...A
N(10)–H(10)...O(30^{i})	0.88	1.95	2.779(5)	155.5
N(13)–H(13A)...O(29^{i})	0.88	2.04	2.858(5)	153.6
N(13)–H(13B)...O(31^{ii})	0.88	2.11	2.950(5)	158.6
N(22)–H(22)...O(28)	0.88	2.05	2.841(5)	148.4
N(25)–H(25A)...O(31)	0.88	2.44	3.251(6)	153.0
N(25)–H(25B)...O(28^{iii})	0.88	2.32	3.116(6)	151.2
O(26)–H(26A)...O(33)	0.85(3)	1.86(3)	2.707(5)	175(5)
O(26)–H(26B)...O(32^{i})	0.85(3)	1.85(3)	2.662(5)	158(5)
O(32)–H(32A)...O(30)	0.86(3)	1.93(3)	2.708(5)	151(5)
O(32)–H(32B)...O(31^{iv})	0.84(3)	1.89(3)	2.735(5)	176(5)
O(33)–H(33)...O(29)	0.84	1.92	2.750(5)	169.0

π-π Interaction[a]	Interplanar distance	Dihedral angle	Centroid offset
[N(14)-N(25)]-[N(14^{viii})-N(25^{viii})]	3.348(10)	0	0.98

[a]Symmetry codes: (i) $x-½, -y+½, z-½$; (ii) $-x+½, y-½, -z+{}^{3}/_{2}$; (iii) $-x+{}^{3}/_{2}, y+½, -z+{}^{3}/_{2}$; (iv) $-x+2, -y+1, -z+2$; (viii) $-x+1, -y+1, -z+1$.

Table S4 Connections making up the hydrogen-bonded network in $[CuBrL_2]Br{\cdot}CH_3OH$ (**1**).[a]

	Distance between nodes (Å)
Cu...Cu pathways [*via* the coordinated bromine atom Br(26)]	
N(13)–H(13B)…Br(26^{i})/N(13^{i})–H(13B^{i})...Br(26)[b]	Cu(1)...Cu(1^{i}) = 7.623(3)
N(25)–H(25B)…Br(26^{iii}) and N(25^{vii})–H(25B^{vii})...Br(26)	Cu(1)...Cu(1^{iii}) = Cu(1)...Cu(1^{vii}) = 7.301(2)
Cu...Br pathways [to the non-coordinated bromine atom Br(27)]	
N(10)–H(10)...Br(27)/N(13)–H(13A)…Br(27)	Cu(1)...Br(27) = 5.5751(19)
N(25)–H(25A)…Br(27^{ii})	Cu(1)...Br(27^{ii}) = 8.458(2)
N(22)–H(22)…O(28)–H(28)…Br(27^{iv})	Cu(1)...Br(27^{iv}) = 5.4041(19)

[a]Symmetry codes correspond to those in Fig. 1 of the main article: (i) $-x+2, -y+1, -z+1$; (ii) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x+\frac{1}{2}, y, -z+\frac{1}{2}$; (iv) $-x+\frac{3}{2}, y+\frac{1}{2}, z$; (vii) $x-\frac{1}{2}, y, -z+\frac{1}{2}$. [b]Centrosymmetric pair.

Table S5 Connections making up the hydrogen-bonded network in $[CuL_2(OH_2)]SO_4{\cdot}H_2O{\cdot}CH_3OH$ (**2**).[a] There are two distinct hydrogen bond pathways linking Cu(1) with S(27) and S(27^{i}).

	Distance between nodes (Å)
Cu...SO_4 pathways	
N(22)–H(22)...O(28)/N(25)–H(25A)...O(31)/O(26)–H(26A)...O(33)–H(33)...O(29)	Cu(1)...S(27) = 5.2754(14)
N(10)–H(10)...O(30^{i})/N(13)–H(13A)...O(29^{i})/ O(26)–H(26B)...O(32^{i})–H(32A^{i})...O(30^{i})	Cu(1)...S(27^{i}) = 5.4879(14)
N(13)–H(13B)…O(31^{ii})	Cu(1)...S(27^{ii}) = 8.3332(14)
N(25)–H(25B)…O(28^{iii})	Cu(1)...S(27^{iii}) = 8.1360(14)
O(26)–H(26B)...O(32^{i})–H(32B^{i})...O(31^{vii})	Cu(1)...S(27^{vii}) = 5.9073(14)
SO_4...SO_4 pathway	
O(30)...H(32A)–O(32)–H(32B)...O(31^{iv})/ O(30^{iv})...H(32A^{iv})–O(32^{iv})–H(32B^{iv})...O(31)[b]	S(27)...S(27^{iv}) = 6.588(3)

[a]Symmetry codes correspond to those in Fig. 2 of the main article: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x+2, -y+1, -z+2$; (vii) $-x+\frac{3}{2}, -y+\frac{1}{2}, -z+\frac{3}{2}$. [b]Centrosymmetric pair.

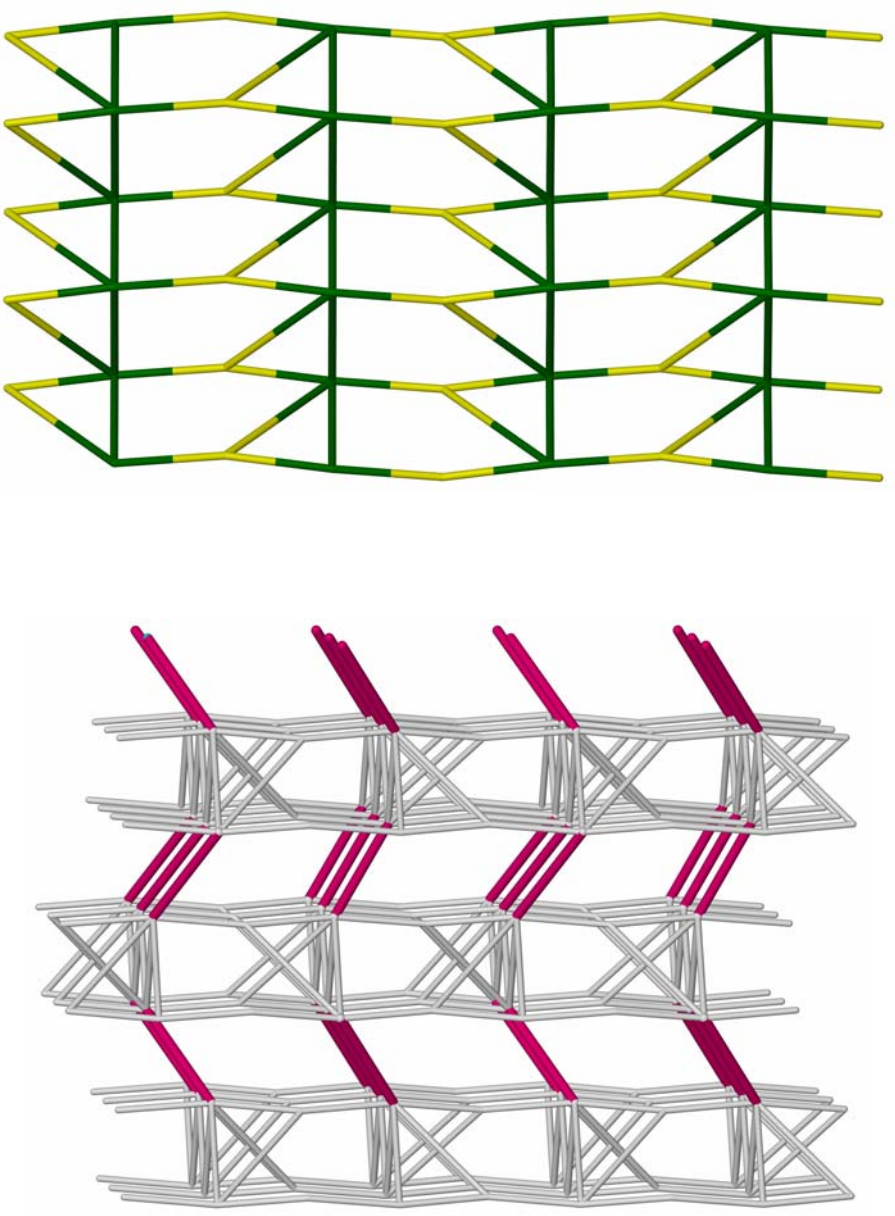

Fig. S2 Two views of the topology of the hydrogen-bonded network in $[CuBrL_2]Br{\cdot}CH_3OH$ (**1**), formed by the hydrogen bonds listed in Table S4. Top: Aggregation of the Cu (green) and Br (yellow) nodes into a zig-zag sheet along the (001) crystal plane, formed from Cu(1)...Cu(1^{iii}) and the three Cu…Br contacts. Bottom: the linking of these sheets (white) into three dimensions by the Cu(1)...Cu(1^{i}) connection (pink).

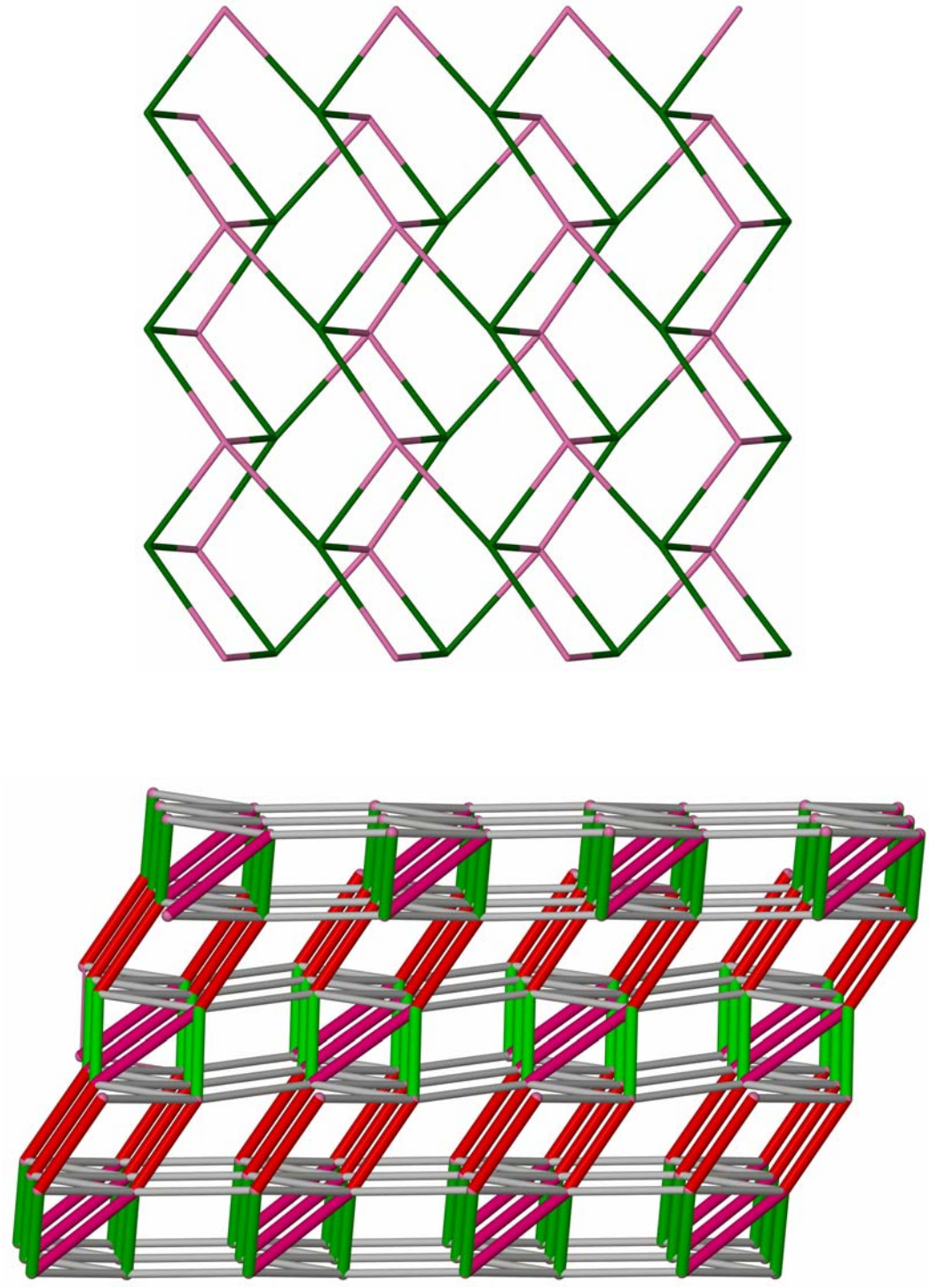

Fig. S3 Two views of the topology of the extended hydrogen-bonded network in $[CuL_2(OH_2)]SO_4{\cdot}H_2O{\cdot}CH_3OH$ (**2**), formed by the hydrogen bonds listed in Table S5. Left: the bilayer of 6^3 sheets formed from the Cu(1)…S(27), Cu(1)…S(27^{ii}) , Cu(1)…S(27^{iii}) and Cu(1)…S(27^{vii}) hydrogen bond pathways, running along the (001) crystal plane. The Cu nodes are in green, and S nodes in pink. Right: the complete network, viewed approximately perpendicular to the (010) plane with the [100] crystal vector horizontal. The layers of 6^3 rings are in white, while the cross-linking pathways are Cu(1)…S(27) (red), Cu(1)…S(27^{i}) (green) and S(27)…S(27^{iv}) (pink).

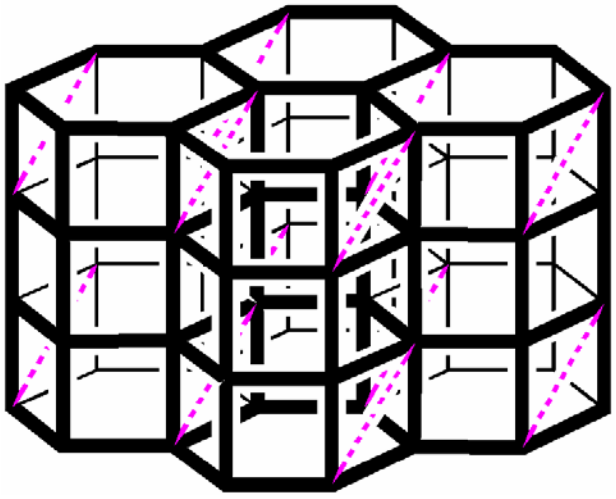

Fig. S4 Diagram showing the relationship between the network topology for $[CuL_2(OH_2)]SO_4 \cdot H_2O \cdot CH_3OH$ (**2**) in Fig. S3, and the boron nitride structure. The BN network is in black, while the additional S(27)…S(27^{iv}) edge (pink in Fig. S3) found in **2** is shown in pink.