Novel hydrogen bond network topologies in complexes of the ditopic ligand 5-amino-3-(pyrid-2-yl)-1*H*-pyrazole

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Table S1 Metric parameters for the hydrogen bond and π-π interactions in $[MnCl_2L_2]\cdot 2CH_3OH$ (**1**·$2CH_3OH$) (Å, °). The symmetry codes correspond to those in Table 1 of the main paper.[a]

Hydrogen bonds	D–H	H...A	D...A	D–H...A
N(11)–H(11)…Cl(2^{ii})	0.875(18)	2.53(2)	3.2771(19)	144(3)
N(14)–H(14A)…Cl(2^{ii})	0.825(17)	2.600(19)	3.344(2)	151(3)
N(14)–H(14B)…O(16)	0.844(17)	2.096(18)	2.902(3)	159(3)
O(16)–H(16)…Cl(2^{iii})	0.934(18)	2.312(19)	3.240(3)	172(3)

π-π Interactions	Interplanar distance	Dihedral angle	Centroid offset
[N(3)-C(13)]-[N(3^{iii})-C(13^{iii})]	3.397(4)	0	1.64

[a]Symmetry codes: (ii) *x*, 1–*y*, ½+*z*; (iii) ½–*x*, ½–*y*, 1–*z*

Table S2 Connections making up the hydrogen-bonded network in $[MnCl_2L_2]\cdot 2CH_3OH$ (**1**·$2CH_3OH$). The symmetry codes correspond to those in Table 1 of the main paper.[a]

	Distance between nodes (Å)
Direct between complex centres [*via* the coordinated chlorine atom Cl(2)]	
N(11)–H(11)…Cl(2^{ii})/N(14)–H(14A)…Cl(2^{ii}) and N(11^{iv})–H(11^{iv})…Cl(2^{i})/N(14^{iv})–H($14A^{iv}$)...Cl(2^{i})[b] N(11^{i})–H(11^{i})…Cl(2^{v})/N(14^{i})–H($14A^{i}$)…Cl(2^{v}) and N(11^{vi})–H(11^{vi})…Cl(2)/N(14^{vi})–H($14A^{vi}$)…Cl(2)[b]	Mn(1)...Mn(1^{iv}) = Mn(1)...Mn(1^{v}) = 7.7576(5)
N(14)–H(14B)…O(16)–H(16)…Cl(2^{iii}) and N(14^{iii})–H($14B^{iii}$)…O(16^{iii})–H(16^{iii})…Cl(2)[b] N(14^{iv})–H($14B^{iv}$)…O(16^{iv})–H(16^{iv})…Cl(2^{vii}) and N(14^{vii})–H($14B^{vii}$)…O(16^{vii})–H(16^{vii})…Cl(2^{iv})[b]	Mn(1)...Mn(1^{iii}) = Mn(1)...Mn(1^{viii}) = 7.9199(2)

[a]Symmetry codes: (i) –*x*, *y*, ½–*z*; (ii) *x*, 1–*y*, ½+*z*; (iii) ½–*x*, ½–*y*, 1–*z*; (iv) –*x*, 1–*y*, 1–*z*; (v) –*x*, 1–*y*, –*z*; (vi) *x*, 1–*y*, –½+*z*; (vii) –½+*x*, ½–*y*, –½+*z*; (viii) –½–*x*, ½–*y*, –*z*.
[b]Centrosymmetric pair.

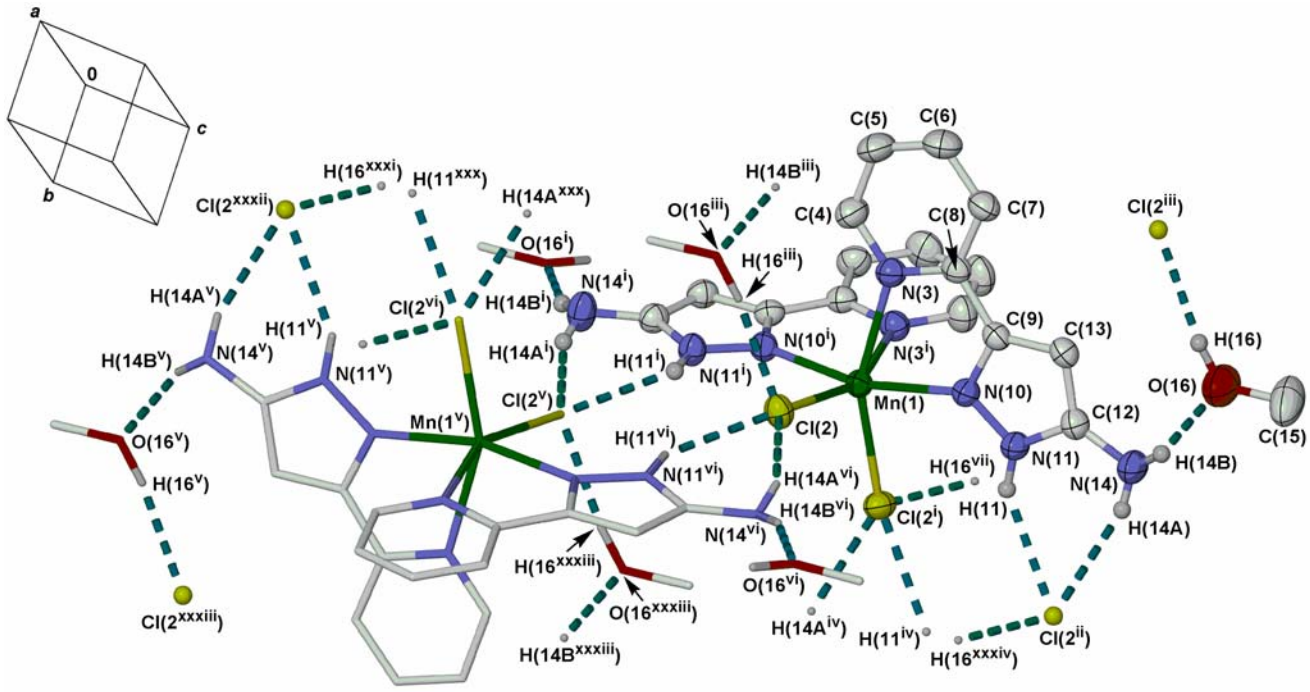

Fig S1 Partial packing diagram of $[MnCl_2L_2]\cdot 2CH_3OH$ (**1**·$2CH_3OH$). All C-bound H atoms have been omitted for clarity. Thermal ellipsoids of the heavy atoms in one of the molecules are at the 50% probability level, while all others have arbitrary radii. The orientation of the unit cell in this view is shown in inset (not to scale). Symmetry codes are listed in Table 1.

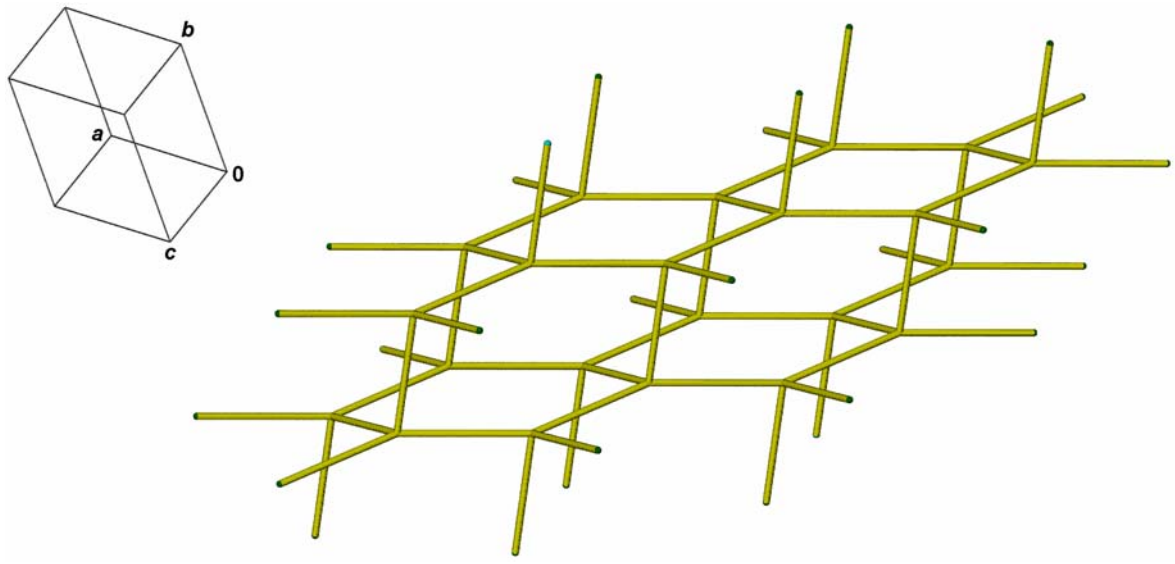

Fig S2 View of the diamond topology of the hydrogen-bond network in $[MnCl_2L_2]\cdot 2CH_3OH$ (**1**·$2CH_3OH$). The vertices correspond to the individual manganese atoms in the structure, which have arbitrary radii, while the connections are those listed in Table S2. All other atoms have been omitted for clarity.

Table S3 Metric parameters for the hydrogen bond and π-π interactions in $[FeCl_2L_2]Cl{\cdot}4CH_3OH$ (**2**·$4CH_3OH$) (Å, °). The symmetry codes correspond to those in Table 1 of the main paper.[a]

Hydrogen bonds	D–H	H...A	D...A	D–H...A
N(12)–H(12)…Cl(2^{ix})	0.876(18)	2.45(2)	3.2493(17)	153(2)
N(15)–H(15A)…Cl(2^{ix})	0.853(18)	2.84(2)	3.556(2)	142(2)
N(15)–H(15A)…O(30^{ix})	0.853(18)	2.46(2)	3.114(3)	134(2)
N(15)–H(15B)…Cl(28)	0.878(18)	2.480(18)	3.355(2)	174(2)
N(24)–H(24)…O(30)	0.899(19)	1.93(2)	2.786(2)	158(2)
N(27)–H(27A)…O(34)	0.880(18)	2.17(2)	3.004(2)	159(2)
N(27)–H(27B)…O(34^{x})	0.872(18)	2.042(19)	2.908(2)	172(2)
O(30)–H(30)…O(32)	0.80(2)	1.91(2)	2.710(2)	173(3)
O(32)–H(32)…Cl(28^{xi})	0.83(2)	2.33(2)	3.1322(17)	162(3)
O(34)–H(34)…Cl(28^{xii})	0.79(2)	2.35(2)	3.1368(16)	172(3)
O(36)–H(36)…Cl(28^{xii})	0.81(2)	2.39(2)	3.197(2)	173(3)

π-π Interactions	Interplanar distance	Dihedral angle	Centroid offset
[N(4)-C(14)]-[N(4^{xii})-C(14^{xii})]	3.331(6)	0	2.91
[N(16)-C(26)]-[N(16^{xiii})-C(26^{xiii})]	3.402(2)	0	1.09

[a]Symmetry codes: (ix) –*x*, –*y*, 1–*z*; (x) 1–*x*, 1–*y*, –*z*; (xi) *x*, 1+*y*, *z*; (xii) 1–*x*, –*y*, 1–*z*; (xiii) –*x*, –*y*, –*z*.

Table S4 Connections making up the hydrogen-bonded network in $[FeCl_2L_2]Cl{\cdot}4CH_3OH$ (**2**·$4CH_3OH$). The symmetry codes correspond to those in Table 1 of the main paper.[a]

	Distance between nodes (Å)
Direct Fe...Fe pathways	
N(12)–H(12)…Cl(2^{ix})/N(15)–H(15A)…Cl(2^{ix})/N(15)–H(15A)…O(30^{ix})...H(24^{ix})–N(24^{ix}) and N(12^{ix})–H(12^{ix})…Cl(2)/ /N(15^{ix})–H($15A^{ix}$)…Cl(2)/N(15^{ix})–H($15A^{ix}$)…O(30)...H(24)–N(24)[b]	Fe(1)...Fe(1^{ix}) = 5.8422(5)
N(27)–H(27A)…O(34)...H(27B^{x})–N(27^{x}) and N(27^{x})–H($27A^{x}$)…O(34^{x})...H(27B)–N(27)[b]	Fe(1)...Fe(1^{x}) = 14.5067(6)
Fe…Cl pathways [to the non-coordinated chlorine atom Cl(28)]	
N(15)–H(15B)…Cl(28)	Fe(1)...Cl(28) = 8.1678(6)
N(24)–H(24)…O(30)–H(30)…O(32)–H(32)...Cl(28^{xi})	Fe(1)...Cl(28^{xi}) = 7.4460(7)
N(27)–H(27A)…O(34)–H(34)…Cl(28^{xii})	Fe(1)...Cl(28^{xii}) = 7.7724(6)
N(27)–H(27B)…O(34^{x})–H(34^{x})…Cl(28^{xiv})	Fe(1)...Cl(28^{xiv}) = 9.3824(6)

[a]Symmetry codes: (ix) –*x*, –*y*, 1–*z*; (x) 1–*x*, 1–*y*, –*z*; (xi) *x*, 1+*y*, *z*; (xii) 1–*x*, –*y*, 1–*z*; (xiv) *x*, 1+*y*, –1+*z*. [b]Centrosymmetric pair.

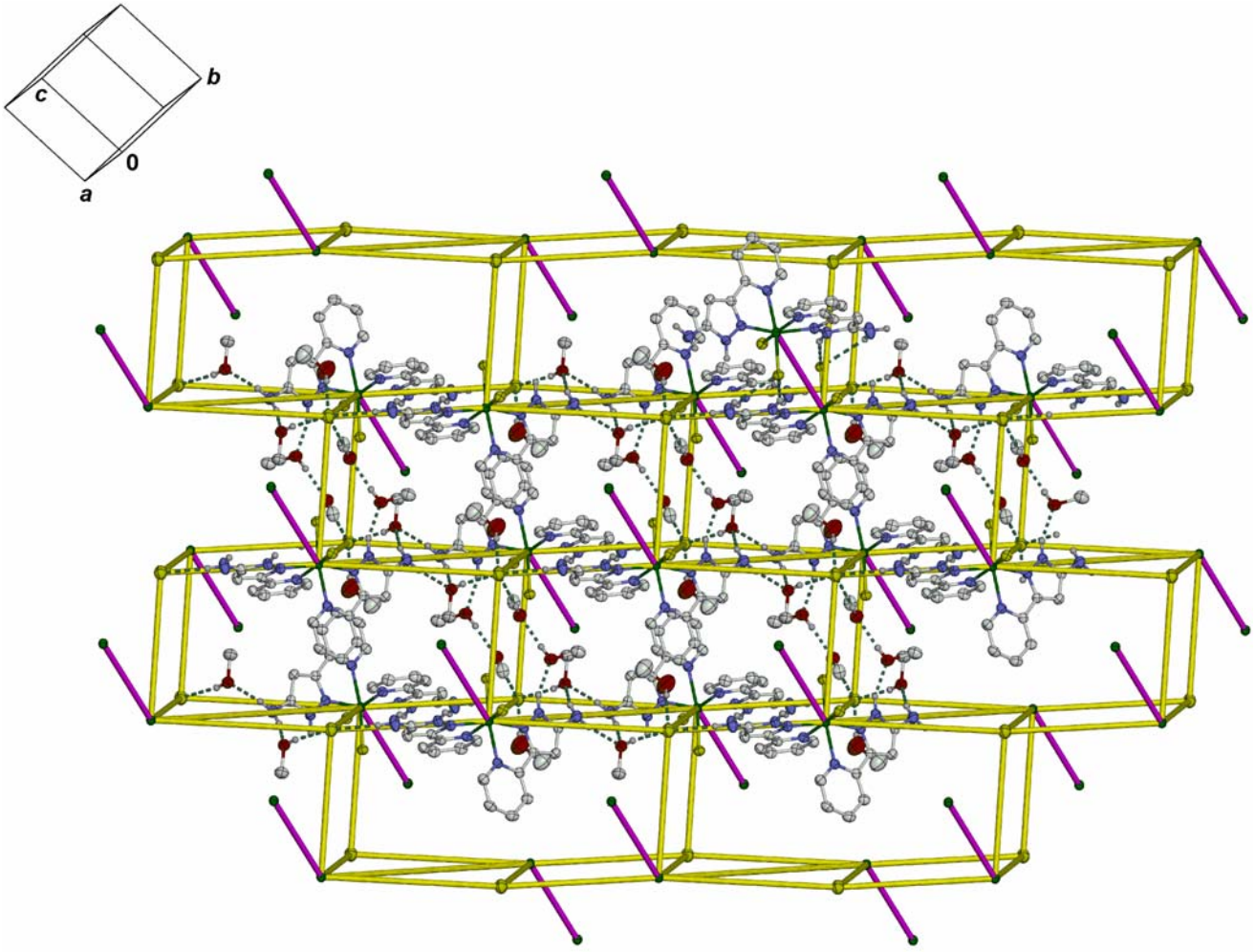

Fig. S3 Partial view of the hydrogen-bonded network topology shown by $[FeCl_2L_2]Cl{\cdot}4CH_3OH$ (**2**·$4CH_3OH$), showing the association of molecules into a hexagonal bilayer structure (yellow) through four Fe–Cl connections, with the additional Fe(1)...Fe(1^{x}) connection bisecting every third square face. The Fe(1)...Fe(1^{ix}) connections, that link these bilayers together in three dimensions, are shown in pink. The network vertices correspond to Fe(1) (green), Cl(28) (yellow) and their symmetry equivalents, and the connections are those listed in Table S4. All atoms have 50% thermal ellipsoids, while all C-bound H atoms have been omitted for clarity. The view is the same as the corresponding part of Fig. 2 of the main paper, and the orientation of the unit cell in this view is shown in inset (not to scale).

Table S5 Metric parameters for the hydrogen bond and π-π interactions in $[Cu(ClO_4)L_2]ClO_4 \cdot CH_3OH$ (**3**·CH_3OH) (Å, °). The data are listed to show the connectivities involved. However, since all the hydrogen bonds in this table involve disordered residues, their metric parameters should be treated with caution. The 'A' and 'B' labels in this table refer to different disorder sites for a particular atom. The symmetry codes correspond to those in Table 1 of the main paper.[a]

Hydrogen bonds	D–H	H...A	D...A	D–H...A
N(10)–H(10)…O(37A)	0.97(2)	1.92(3)	2.881(11)	167(5)
N(10)–H(10)…O(37B)	0.97(2)	1.70(3)	2.640(11)	160(5)
N(13)–H(13A)…O(29A)	0.98(2)	2.11(4)	2.975(7)	146(5)
N(13)–H(13A)…O(27B)	0.98(2)	2.36(4)	3.32(3)	167(4)
N(13)–H(13B)…O(30A^{xv})	0.98(2)	2.24(3)	3.179(10)	161(5)
N(13)–H(13B)…O(30B^{xv})	0.98(2)	2.18(4)	3.10(3)	155(5)
N(22)–H(22)…O(30A^{xvi})	0.97(2)	1.91(3)	2.879(9)	172(5)
N(22)–H(22)…O(30B^{xvi})	0.97(2)	2.07(4)	3.02(3)	166(5)
N(25)–H(25A)…O(28A^{xvi})	0.97(2)	2.15(3)	3.086(7)	161(4)
N(25)–H(25A)…O(28B^{xvi})	0.97(2)	2.12(4)	3.06(2)	160(4)
N(25)–H(25B)…O(35A^{xvii})	0.97(2)	2.29(3)	3.167(8)	151(4)
N(25)–H(25B)…O(35B^{xvii})	0.97(2)	2.45(4)	3.329(16)	151(4)
O(37A)–H(37A)…O(27A)	0.84	2.16	3.002(11)	174.4
O(37A)–H(37A)…O(27B)	0.84	2.35	3.11(3)	150.9
O(37B)–H(37B)…O(35A)	0.84	1.93	2.668(11)	146.2
O(37B)–H(37B)…O(35B)	0.84	1.93	2.694(16)	151.2

π-π Interactions	Interplanar distance	Dihedral angle	Centroid offset
[N(2)-C(12)]-[N(2^{xviii})-C(12^{xviii})]	3.44(2)	0	1.66
[N(2)-C(12)]-[N(2^{iv})-C(12^{iv})]	3.43(2)	0	3.21
[N(14)-C(24)]-[N(14^{xix})-C(24^{xix})]	3.174(19)[b]	10.13(4)	5.44
[N(14)-C(24)]-[N(14^{xvii})-C(24^{xvii})]	3.533(17)[b]	10.13(4)	5.21

[a]Symmetry codes: (iv) $-x$, $1-y$, $1-z$; (xv) $1-x$, $1-y$, $2-z$; (xvi) $-1+x$, y, $-1+z$; (xvii) x, $^3/_2-y$, $-½+z$; (xviii) $1-x$, $1-y$, $1-z$; (xix) 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 S6 Connections making up the hydrogen-bonded network in $[Cu(ClO_4)L_2]ClO_4{\cdot}CH_3OH$ (**3**$\cdot CH_3OH$).[a] For clarity, only the 'A' disorder sites of the disordered residues in the structure are considered. The connectivity is the same if the 'B' disorder orientations are used instead, although the distances between nodes are slightly different. The symmetry codes correspond to those in Table 1 of the main paper.[a]

	Distance between nodes (Å)
Direct Cu...Cu pathways [*via* the coordinated perchlorate ion Cl(31)-O(35)]	
N(25)–H(25B)…O(35A^{xvii})–Cl(31A^{xvii})/ N(25^{xix})–H(25B^{xix})…O(35A)–Cl(31A)	Cu(1)...Cu(1^{xvii}) = Cu(1)...Cu(1^{xix}) = 9.4232(8)
Cu…ClO_4 pathways [to the non-coordinated perchlorate ion Cl(26)-O(30)]	
N(10)–H(10)…O(37A)–H(37A)…O(27A) and N(13)–H(13A)…O(34)–H(34)…O(29A)	Cu(1)...Cl(26A) = 6.4029(15)
N(13)–H(13B)…O(30A^{xv})	Cu(1)...Cl(26A^{xv}) = 8.7863(16)
N(22)–H(22)…O(30A^{xvi}) and N(25)–H(25A)…O(28A^{xvi})	Cu(1)...Cl(26A^{xvi}) = 5.8121 (15)

[a]Symmetry codes: (xv) 1–*x*, 1–*y*, 2–*z*; (xvi) –1+*x*, *y*, –1+*z*; (xvii) *x*, $^3/_2$–*y*, –½+*z*; (xix) *x*, $^3/_2$–*y*, ½+*z*.

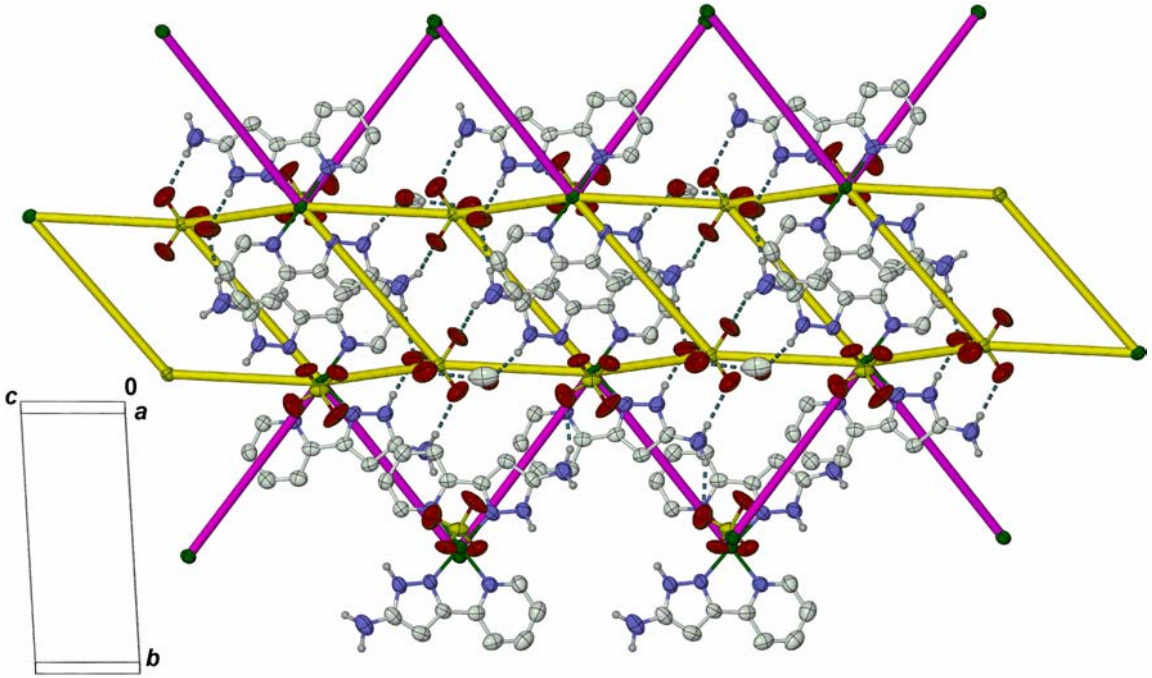

Fig S4 Partial view of the hydrogen-bonded network topology shown by $[Cu(ClO_4)L_2]ClO_4{\cdot}CH_3OH$ (**3**$\cdot CH_3OH$), showing the association of molecules into a 1-D ladder structure formed by the three unique Cu(1)…Cl(26)-O(31) connections (yellow). The Cu(1)…Cu(1) connections that link these ladders together are shown in pink. Only the 'A' orientations of the disordered residues in the structure are shown. The network vertices correspond to Cu(1) and Cl(26A) and their symmetry equivalents, and the connections are those listed in Table S6. All atoms have 50% thermal ellipsoids, while all C-bound H atoms have been omitted for clarity. The view is the same as the corresponding part of Fig. 5 of the main paper, and the orientation of the unit cell in this view is shown in inset (not to scale).

Table S7 Metric parameters for the hydrogen bond and π-π interactions in $[Cu(NCMe)L_2][ClO_4]_2$ (**4**) (Å, °). The symmetry codes correspond to those in Table 1 of the main paper.[a]

Hydrogen bonds[a]	D–H	H...A	D...A	D–H...A
N(10)–H(10)…O(18)	0.86(2)	2.34(4)	2.988(4)	133(4)
N(13)–H(13A)…O(19)	0.85(2)	2.18(3)	3.026(5)	171(4)
N(13)–H(13B)…O(19^{xxi})	0.86(2)	2.12(3)	2.956(4)	166(4)

π-π Interactions[a]	Interplanar distance	Dihedral angle	Centroid offset
[N(2)-C(12)]-[N(2^{iv})-C(12^{iv})]	3.525(11)	0	1.40

[a]Symmetry codes: (iv) –*x*, 1–*y*, 1–*z*; (xxi) –½–*x*, ³/₂–*y*, 1–*z*.

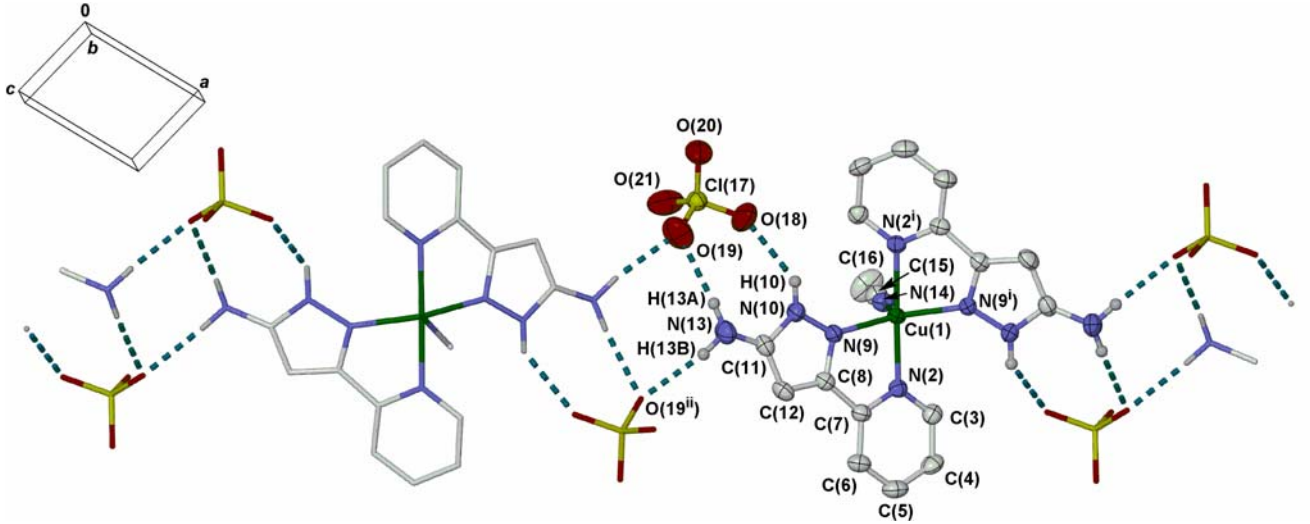

Fig S5 Partial packing diagram of $[Cu(NCMe)L_2][ClO_4]_2$ (**4**), showing its organisation into 1-D hydrogen-bonded chains. Thermal ellipsoids of the heavy atoms in one of the molecules are at the 50% probability level, while all others have arbitrary radii. The orientation of the unit cell in this view is shown in inset (not to scale). Symmetry codes are listed in Table 1.

Table S8 Metric parameters for the hydrogen bond and π-π interactions in isostructural $[Cu(NO_3)L_2]NO_3{\cdot}xH_2O$ (**5**·xH$_2$O) and $[Zn(NO_3)L_2]NO_3{\cdot}xH_2O$ (**6**·xH$_2$O) (Å, °). The data for **6**·xH$_2$O are in square brackets. The 'A' and 'B' labels refer to the two different formula units in the asymmetric unit of these structures, while N(30A)-O(33A) and N(30C)-O(33C) are different disorder sites for the same nitrate anion. The symmetry codes correspond to those in Table 1 of the main paper.[a]

Hydrogen bonds	D–H	H...A	D...A	D–H...A
N(10A)–H(10A)…O(33B^{xxii})	0.850(14) [0.898(14)]	2.02(2) [1.987(16)]	2.845(6) [2.872(4)]	163(4) [168(4)]
N(13A)–H(13A)…O(31B^{xxii})	0.837(14) [0.890(14)]	2.153(19) [2.222(17)]	2.949(7) [3.065(5)]	159(4) [158(3)]
N(13A)–H(13A)…O(27B^{xxii})	0.837(14) [0.890(14)]	2.70(3) [2.61(3)]	2.976(5) [2.920(4)]	101(3) [101(2)]
N(13A)–H(13B)…O(27B^{xxii})	0.837(14) [0.885(13)]	2.53(3) [2.57(3)]	2.976(5) [2.920(4)]	114(3) [104(2)]
N(13A)–H(13B)…O(32B^{xxiii})	0.837(14) [0.885(13)]	2.69(2) [2.576(19)]	3.400(7) [3.346(5)]	143(3) [146(3)]
N(22A)–H(22A)…O(34A)[b]	0.837(14) [0.896(14)]	2.14(3) [1.989(19)]	2.924(12) [2.848(5)]	155(4) [160(4)]
N(22A)–H(22A)…O(31C)[b]	0.837(14) [0.896(14)]	2.35(3) [2.35(3)]	3.051(6) [3.094(8)]	142(4) [140(3)]
N(25A)–H(25A)…O(32A)[b]	0.841(14) [0.886(13)]	2.24(3) [2.253(19)]	3.06(3) [3.110(8)]	166(4) [163(3)]
N(25A)–H(25A)…O(32C)[b]	0.841(14) [0.886(13)]	2.082(19) [2.06(2)]	2.912(9) [2.936(14)]	169(3) [169(4)]
N(25A)–H(25B)…O(29B)	0.835(14) [0.894(13)]	2.26(2) [2.17(2)]	3.035(5) [2.967(4)]	154(3) [148(3)]
O(34A)…O(28A)[b,c]	-	-	2.467(13) [2.883(5)]	-
O(34A)…O(31A)[b,c]	-	-	2.738(19) [2.717(6)]	-
N(10B)–H(10B)…O(31B)	0.846(14) [0.892(14)]	2.02(3) [1.914(18)]	2.748(5) [2.780(4)]	144(4) [163(4)]
N(13B)–H(13C)…O(32B)	0.841(11) [0.882(11)]	2.190(17) [2.203(17)]	2.997(5) [3.024(4)]	161(2) [154.8(17)]
N(13B)–H(13D)…O(29B^{xxiv})	0.836(11) [0.884(11)]	2.56(2) [2.52(2)]	3.105(5) [3.074(4)]	124(3) [121(2)]
N(13B)–H(13D)…O(31A^{xxv})[b]	0.836(11) [0.884(11)]	2.18(3) [2.20(2)]	2.897(18) [2.980(6)]	144(4) [147(3)]
N(22B)–H(22B)…O(33A^{xxvi})[b]	0.842(14) [0.896(14)]	1.84(3) [1.856(19)]	2.67(2) [2.725(7)]	171(4) [163(4)]
N(22B)–H(22B)…O(33C^{xxvi})[b]	0.842(14) [0.896(14)]	2.13(2) [2.12(2)]	2.942(7) [2.983(13)]	161(4) [161(3)]
N(25B)–H(25C)…O(32A^{xxvi})[b]	0.840(14) [0.890(14)]	2.44(3) [2.53(2)]	3.16(3) [3.294(9)]	144(4) [145(3)]
N(25B)–H(25C)…O(32C^{xxvi})[b]	0.840(14) [0.890(14)]	2.29(2) [2.23(2)]	3.046(9) [3.037(14)]	151(4) [150(3)]
N(25B)–H(25D)…O(34A^{xxvii})[b]	0.844(14) [0.917(14)]	1.84(2) [1.93(2)]	2.670(13) [2.800(6)]	166(5) [158(4)]

π-π Interactions	Interplanar distance	Dihedral angle	Centroid offset
[N(2A)-C(12A)]-[N(14B^{x})-C(24B^{x})]	3.641(18) [3.574(14)][d]	10.00(7) [11.14(5)]	2.61 [2.89]
[N(2B)-C(12B)]-[N(2B^{x})-C(12B^{x})]	3.260(16) [3.291(13)]	0 [0]	1.28 [1.38]

[a]Symmetry codes: (x) 1–x, 1–y, –z; (xxii) $^3/_2$–x, 1–y, ½+z; (xxiii) x, ½–y, ½+z; (xxiv) $^3/_2$–x, –½+y, z; (xxv) –½+x, ½–y, –z; (xxvi) $^3/_2$–x, ½+y, z; (xxvii) –½+x, $^3/_2$–y, –z. [b]These interactions involve disordered residues, and their metric parameters should be treated with caution. [c] H atoms on water molecule O(34) were not located. [d]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 S9 Connections making up the hydrogen-bonded networks in $[Cu(NO_3)L_2]NO_3{\cdot}xH_2O$ (**5**$\cdot x$$H_2O$) and $[Zn(NO_3)L_2]NO_3{\cdot}xH_2O$ (**6**$\cdot x$$H_2O$), when the 'A' disorder sites of the disordered nitrate ion and water molecule in the structure are considered. The connections given in italics are not present if the alternative disorder orientation N(30C)-O(33C) is used instead, and O(34A) is missing. The distances between nodes involving anion N(30A/C)-O(33A/C) are also slightly different in that case. The symmetry codes correspond to those in Table 1 of the main paper.[a]

	Distance between nodes (Å)
Direct M...M pathways between 'A' and 'B' molecules	
N(13A)–H(13A)…O(27B^{xxii})/N(13A)–H(13B)…O(27B^{xxii})	M(1A)...M(1B^{xxii}) = 8.6903(7) [8.7143(5)]
N(25A)–H(25B)…O(29B)	M(1A)...M(1B) = 9.7160(7) [9.9557(5)]
N(25B)–H(25D)…O(34A^{xxvii})–H...O(28A^{xxvii})	*M(1B)...M(1A^{xxvii}) = 8.3845(7) [8.5059(5)]*
Direct M...M pathways between symmetry equivalents of the same molecule	
N(13B)–H(13D)…O(29B^{xxiv}) and N(13B^{xxvi})–H(13D^{xxvi})…O(29B)	M(1B)...M(1B^{xxiv}) = M(1B)...M(1B^{xxvi}) = 9.6752(6) [9.5063(4)]
M…NO_3 pathways	
N(22A)–H(22A)…O(34A)...O(31A)/N(25A)–H(25A)…O(32A)	M(1A)...N(30A) = 6.42(2) [6.397(8)]
N(10A)–H(10A)...O(33B^{xxii})/N(13A)–H(13A)…O(31B^{xxii})	M(1A)...N(30B^{xxii}) = 5.510(5) [5.431(3)]
N(13A)–H(13B)…O(32B^{xxiii})	M(1A)...N(30B^{xxiii}) = 7.687(5) [7.886(3)]
N(10B)–H(10B)...O(31B)/N(13B)–H(13C)…O(32B)	M(1B)...N(30B) = 5.650(4) [5.573(3)]
N(13B)–H(13D)…O(31A^{xxv})	*M(1B)...N(30A^{xxv}) = 7.920(19) [8.123(9)]*
N(22B)–H(22B)…O(33A^{xxvi})/N(25B)–H(25C)…O(32A^{xxvi})	M(1B)...N(30A^{xxvi}) = 5.151(19) [5.268(8)]
N(25B)–H(25D)…O(34A^{xxvii})–H...O(31A^{xxvii})	*M(1B)...N(30A^{xxvii}) = 9.086(19) [9.175(9)]*

[a]Symmetry codes: (x) 1–x, 1–y, –z; (xxii) $^3/_2$–x, 1–y, ½+z; (xxiii) x, ½–y, ½+z; (xxiv) $^3/_2$–x, –½+y, z; (xxv) –½+x, ½–y, –z; (xxvi) $^3/_2$–x, ½+y, z; (xxvii) –½+x, $^3/_2$–y, –z.

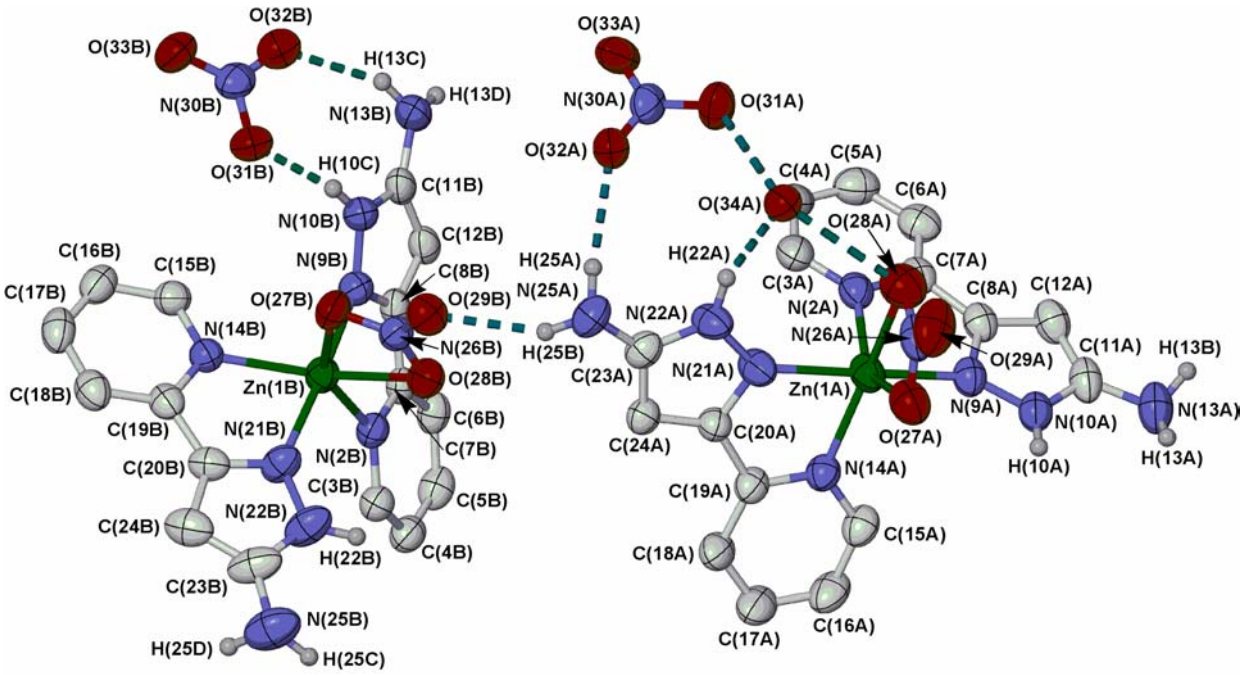

Fig S6 View of the complete asymmetric unit of $[Zn(NO_3)L_2]NO_3{\cdot}xH_2O$ (**6**·*x*H_2O), showing the atom numbering scheme employed. For clarity, only the 'A' disorder orientation of atoms N(30A)-O(34A) is shown, and all C-bound H atoms have been omitted for clarity. All thermal ellipsoids are at the 50% probability level, except for H atoms which have arbitrary radii. The structure of $[Cu(NO_3)L_2]NO_3{\cdot}xH_2O$ (**5**·*x*H_2O) is visually very similar to this one, and uses an identical atom numbering scheme but with Zn(1A) and Zn(1B) replaced by Cu(1A) and Cu(1B).

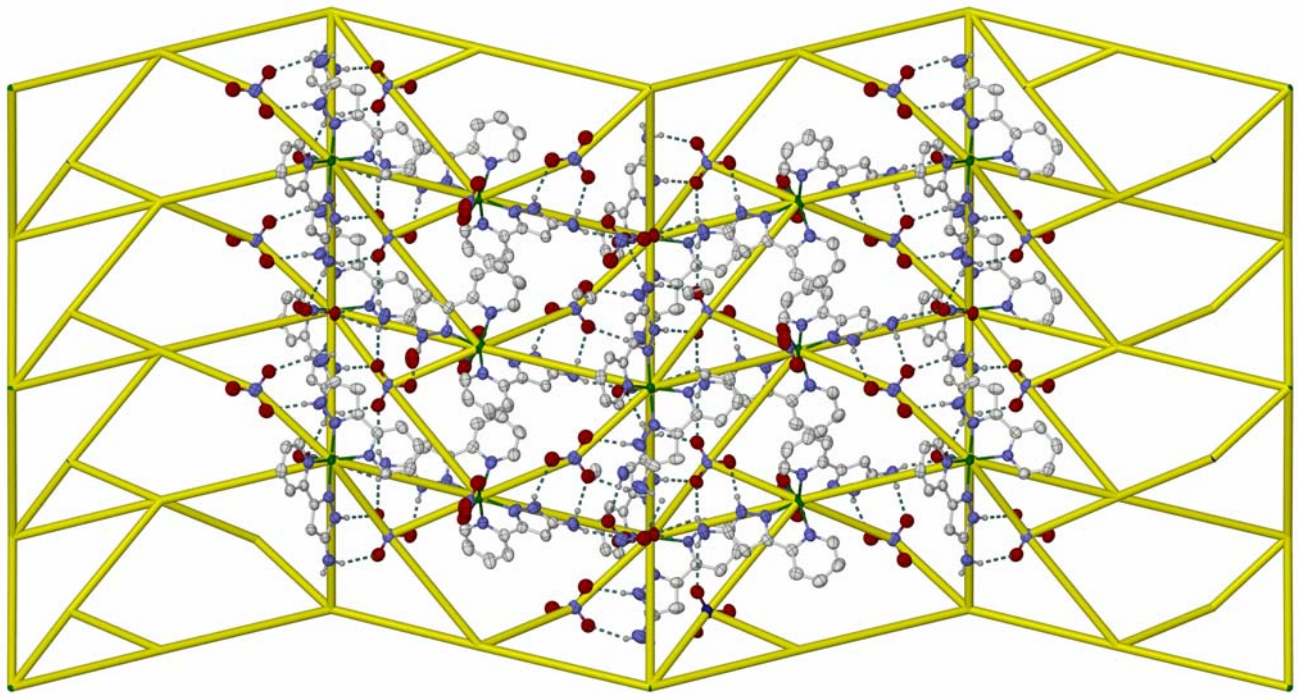

Fig S7 View of the two-dimensional hydrogen-bond network in $[Zn(NO_3)L_2]NO_3{\cdot}xH_2O$ (**6**·*x*H_2O), in the absence of partial water molecule O(34A). The network vertices correspond to Zn(1A), Zn(1B), N(30B) and their symmetry equivalents, and the connections are those listed in Table S9 (excluding those in italics). All atoms have 50% thermal ellipsoids, while all C-bound H atoms have been omitted for clarity. The view is the same as the corresponding part of Fig. 7 of the main paper, being exactly parallel to the (100) crystal plane with *c* horizontal.

Table S10 Metric parameters for the hydrogen bonds in $[Cu_2(L–H)_4]\cdot xH_2O$ (**7**$\cdot xH_2O$) (Å, °). Symmetry codes correspond to those in Fig. 1 of the main paper. There are no π-π interactions in this structure. The symmetry codes correspond to those in Table 1 of the main paper.[a]

Hydrogen bonds	D–H	H...A	D...A	D–H...A
N(14)–H(14A)…N(47)	0.87(3)	2.09(3)	2.944(7)	167(5)
N(26)–H(26A)…N(35)	0.88(3)	2.20(3)	3.073(6)	171(5)
N(26)–H(26B)…N(50^{xxviii})	0.88(3)	2.32(3)	3.148(6)	157(5)
N(38)–H(38B)…N(14^{xxix})	0.88(3)	2.26(4)	3.069(6)	154(6)

[a]Symmetry codes: (xxviii) 2–*x*, ½+*y*, ½–*z*; (xxix) –1+*x*, *y*, *z*.

Table S11 Connections making up the hydrogen-bonded network in $[Cu_2(L–H)_4]\cdot xH_2O$ (**7**$\cdot xH_2O$; $x \approx 0.25$). The 'X' node corresponds to the midpoint of the Cu(1)…Cu(2) vector. The symmetry codes correspond to those in Table 1 of the main paper.[a]

	Distance between nodes (Å)
N(26)–H(26B)…N(50^{xxviii}) and N(26)–H(26B^{xxxviii})…N(50)	X(1)...X(1^{xxviii}) = X(1)...X(1^{xxxviii}) = 9.279
N(38)–H(38B)…N(14^{xxix}) and N(3 ^{xxxix})–H(38B^{xxxix})…N(14)	X(1)...X(1^{xxix}) = X(1)...X(1^{xxxix}) = 12.375

[a]Symmetry codes: (xxviii) 2–*x*, ½+*y*, ½–*z*; (xxix) –1+*x*, *y*, *z*; (xxxviii) 2–*x*, –½+*y*, ½–*z*; (xxxix) 1+*x*, *y*, *z*.

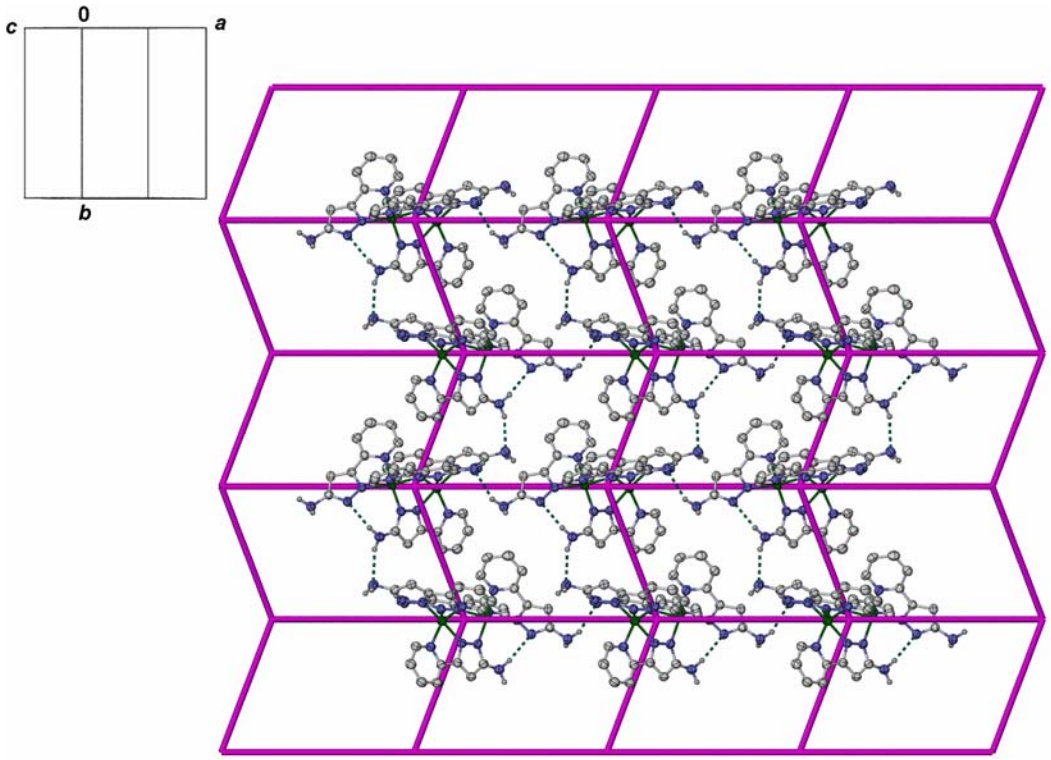

Fig S8 View of the two-dimensional 4^4 hydrogen-bond network in $[Cu_2(L–H)_4]\cdot xH_2O$ (**7**$\cdot xH_2O$). The network vertices correspond to the centroids between the two copper ions in each molecule and have arbitrary radii, while the connections are those listed in Table S11. All other atoms have 50% thermal ellipsoids while all C-bound H atoms have been omitted for clarity. The orientation of the unit cell in this view is shown in inset (not to scale).