Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis and Coordination Chemistry of 1,1,1-*Tris*-(pyrid-2-yl)ethane

Amedeo Santoro,* Carlo Sambiagio,
Patrick C. McGowan and Malcolm A. Halcrow*

School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, UK LS2 9JT.

E-mails: a.santoro@leeds.ac.uk
m.a.halcrow@leeds.ac.uk

Supporting Information

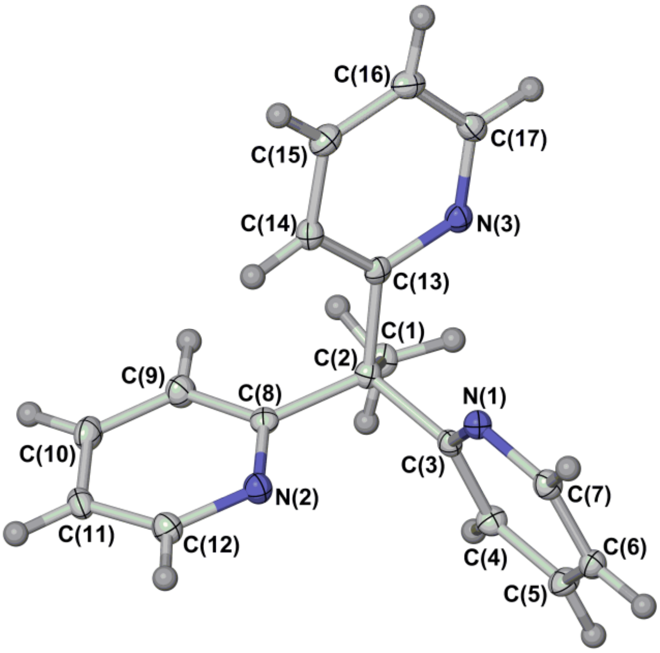

Figure S1 View of the asymmetric unit in the crystal structure of *L*. Displacement ellipsoids are drawn at the 50 % probability level, except for H atoms which have arbitrary radii.

Colour code: C, white; H, pale grey; N, blue.

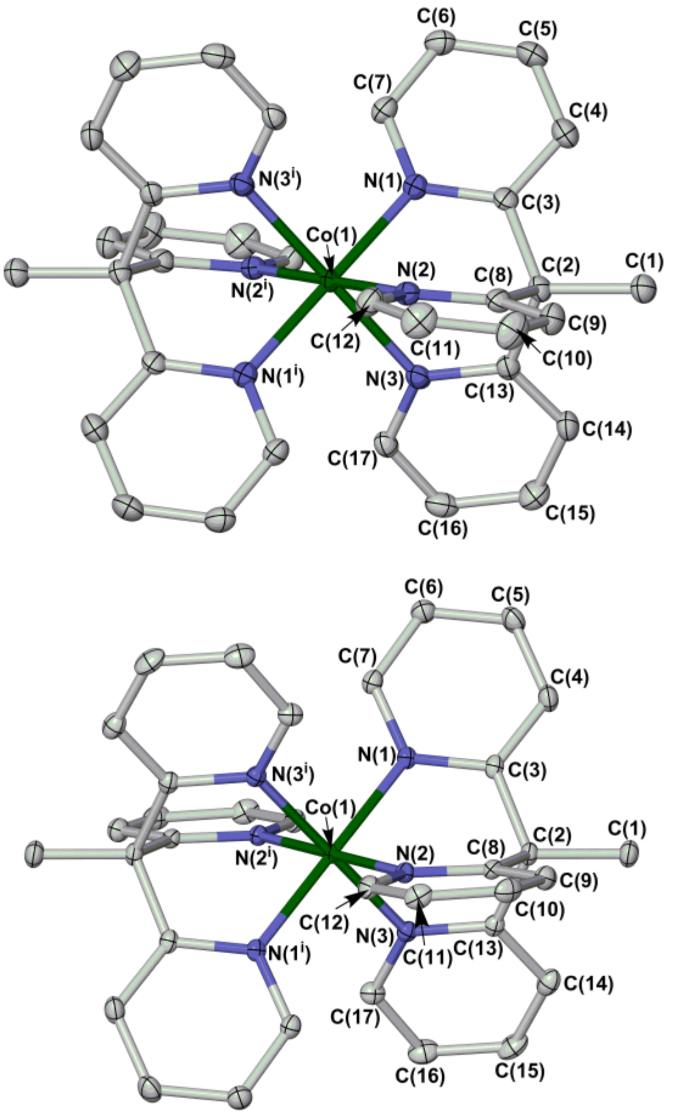

Figure S2 Views of the complex cations in the crystal structures of **2**·4MeCN (top) and **3**·4MeCN (bottom). Displacement ellipsoids are drawn at the 50 % probability level, and H atoms have been omitted for clarity. Symmetry code (i) –*x*, 1–*y*, 1–*z*.

Colour code: C, white; H, pale grey; N, blue. Metric parameters for these two structures are listed in Table 1 in the main article.

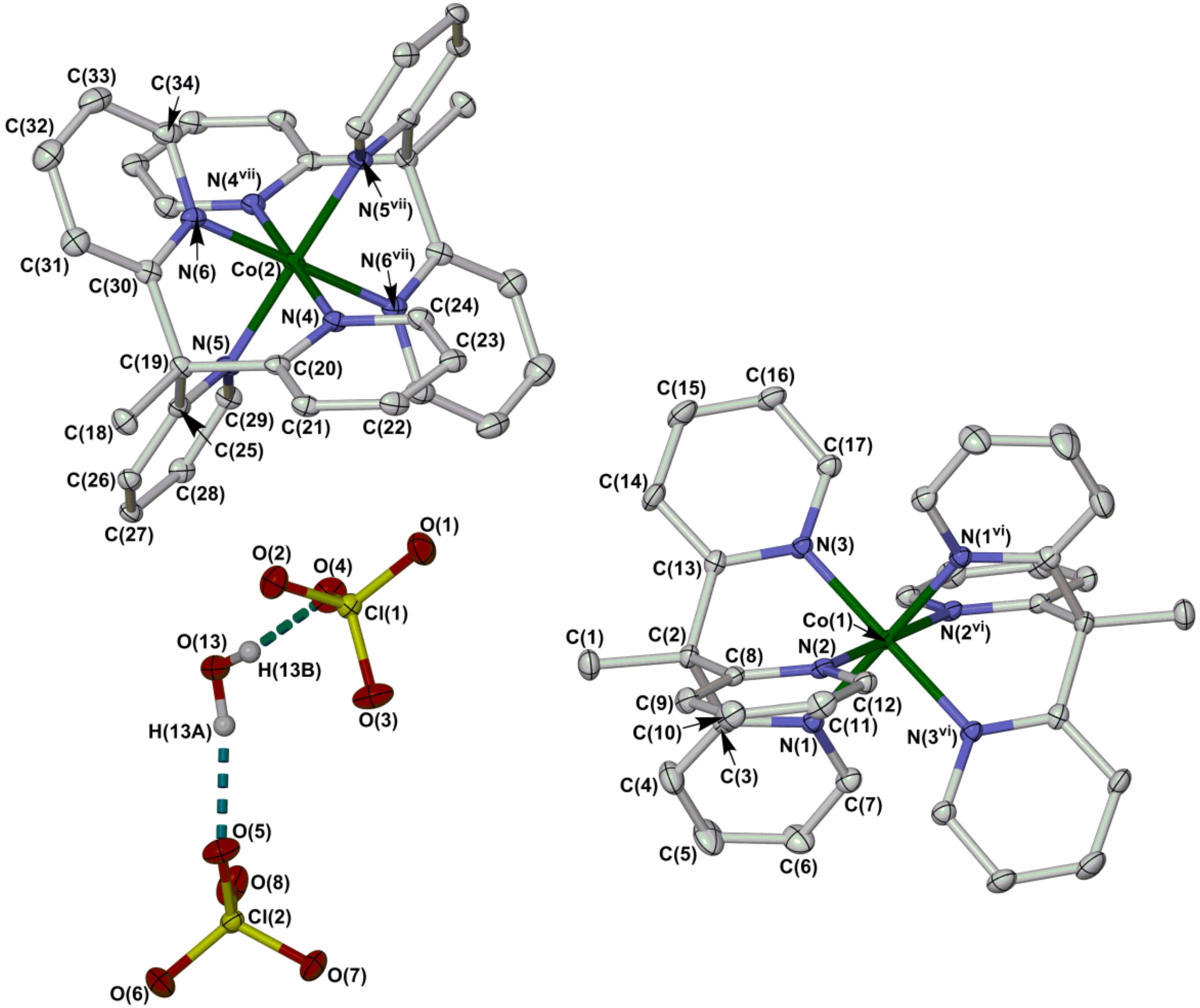

Figure S3 View of the formula unit in the crystal structure of **3**·H_2O. Displacement ellipsoids are drawn at the 50 % probability level, and C-bound H atoms have been omitted for clarity. The disordered ClO_4^- ion does not participate in hydrogen bonding, and is also not shown. Symmetry codes: (vi) 2–*x*, 2–*y*, 2–*z*; (vii) 1–*x*, 2–*y*, 1–*z*.

Colour code: C, white; H, pale grey; Cl, yellow; Co, green; N, blue; O, red.

Table S1 Selected bond distances and angles in the crystal structure of **3**·H_2O (Å, °). See Fig. S3 for the atom numbering scheme employed. Data for the solvate **3**·4MeCN are given in the main article.[a]

Co(1)–N(1)	1.953(2)	Co(2)–N(4)	1.920(2)
Co(1)–N(2)	1.936(2)	Co(2)–N(5)	1.932(2)
Co(1)–N(3)	1.942(2)	Co(2)–N(6)	1.952(2)
N(1)–Co(1)–N(1^{vi})	180	N(4)–Co(2)–N(4^{vii})	180
N(1)–Co(1)–N(2)	89.07(10)	N(4)–Co(2)–N(5)	89.03(9)
N(1)–Co(1)–N(2^{vi})	90.93(10)	N(4)–Co(2)–N(5^{vii})	90.97(9)
N(1)–Co(1)–N(3)	89.12(10)	N(4)–Co(2)–N(6)	89.41(10)
N(1)–Co(1)–N(3^{vi})	90.88(10)	N(4)–Co(2)–N(6^{vii})	90.59(10)
N(2)–Co(1)–N(2^{vi})	180	N(5)–Co(2)–N(5^{vii})	180
N(2)–Co(1)–N(3)	88.83(9)	N(5)–Co(2)–N(6)	89.30(10)
N(2)–Co(1)–N(3^{vi})	91.17(9)	N(5)–Co(2)–N(6^{vii})	90.70(10)
N(3)–Co(1)–N(3^{vi})	180	N(6)–Co(2)–N(6^{vii})	180

[a] Symmetry codes: (vi) 2–*x*, 2–*y*, 2–*z*; (vii) 1–*x*, 2–*y*, 1–*z*.

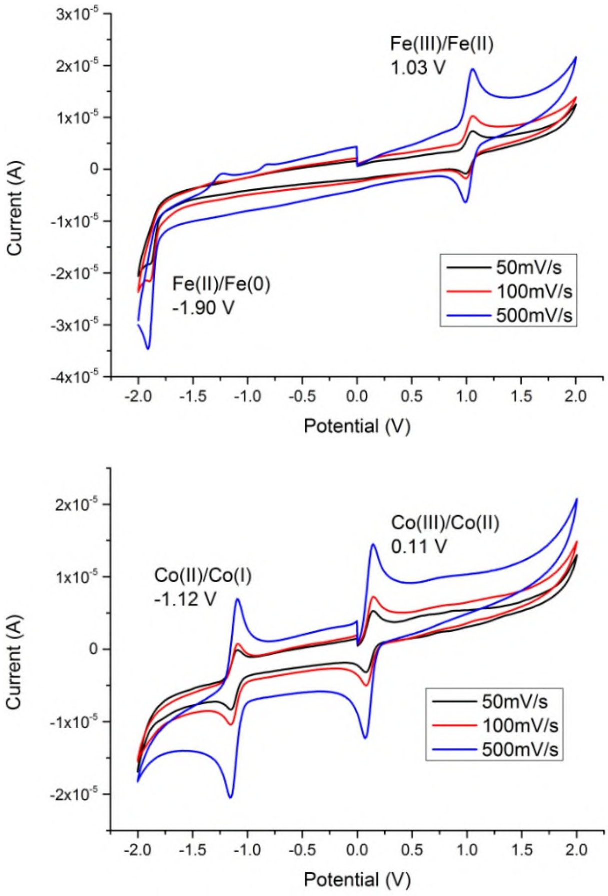

Figure S4 Cyclic voltammograms for **1** (top) and **2** (bottom) in MeCN/0.1 M NBu_4ClO_4 at 298 K, at three different scan rates. Potentials are referenced against an Ag/AgCl reference electrode ($E_{½}$ for Fc/Fc^+ under these conditions = +0.42 V).

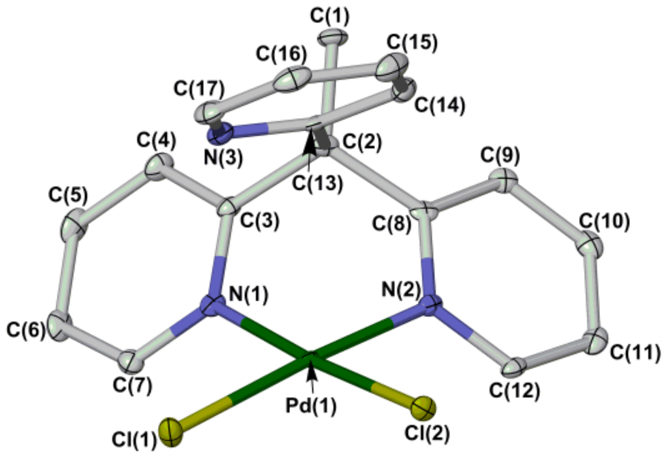

Figure S5 View of the asymmetric unit in the crystal structure of **4**. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms have been omitted for clarity.

Colour code: C, white; Cl, yellow; N, blue; Pd, green.

Table S2 Selected bond distances and angles in the crystal structure of **4** (Å, º). See Fig. S5 for the atom numbering scheme employed.

Pd(1)–Cl(1)	2.2988(6)	Pd(1)–N(1)	2.035(2)
Pd(1)–Cl(2)	2.2965(5)	Pd(1)–N(2)	2.027(2)
Cl(1)–Pd(1)–Cl(2)	90.46(2)	Cl(2)–Pd(1)–N(1)	175.90(6)
Cl(1)–Pd(1)–N(1)	91.82(6)	Cl(2)–Pd(1)–N(2)	91.52(6)
Cl(1)–Pd(1)–N(2)	174.70(6)	N(1)–Pd(1)–N(2)	86.50(8)

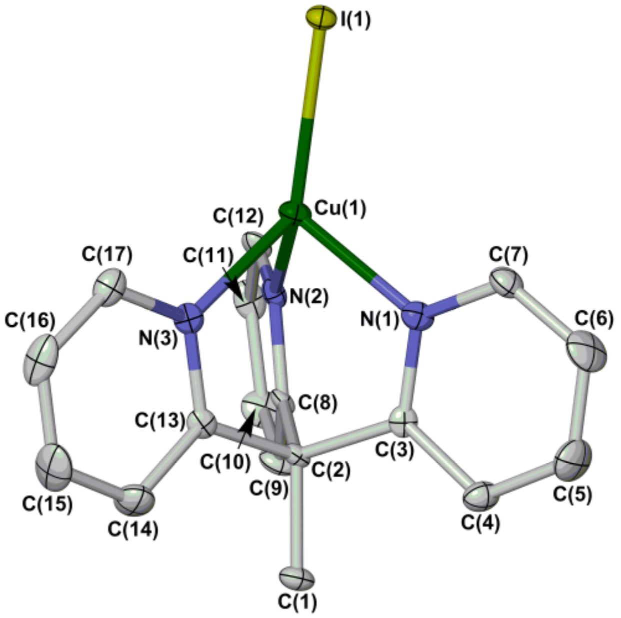

Figure S6 View of the asymmetric unit in the crystal structure of **6**·0.5MeCN. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms have been omitted for clarity.

Colour code: C, white; Cu, green; I, yellow; N, blue.

Table S3 Selected bond distances and angles in the crystal structure of **6**·0.5MeCN (Å, º). See Fig. S6 for the atom numbering scheme employed.

Cu(1)–I(1)	2.4796(7)	Cu(1)–N(2)	2.051(4)
Cu(1)–N(1)	2.067(4)	Cu(1)–N(3)	2.056(4)
I(1)–Cu(1)–N(1)	117.78(12)	N(1)–Cu(1)–N(2)	91.40(16)
I(1)–Cu(1)–N(2)	129.11(11)	N(1)–Cu(1)–N(3)	88.07(16)
I(1)–Cu(1)–N(3)	129.97(12)	N(2)–Cu(1)–N(3)	88.35(16)

Table S4 Selected bond distances and angles in the crystal structure of **7b**·4dmf·0.4H_2O (Å, º). See Fig. 5 of the main article for the atom numbering scheme employed.

Cu(1)–N(1)	2.050(5)	Cu(2)–N(4)	1.988(5)
Cu(1)–N(2)	2.024(5)	Cu(2)–N(5)	1.988(5)
Cu(1)–N(3)	2.155(5)	Cu(2)–N(6)	2.239(5)
Cu(1)–I(1)/O(1)	2.5102(17)/ 2.031(10)	Cu(2)–O(3)	1.994(4)
Cu(1)–O(2)	1.947(4)	Cu(2)–O(4)	1.996(4)
N(1)–Cu(1)–N(2)	83.5(2)	N(4)–Cu(2)–N(5)	88.4(2)
N(1)–Cu(1)–N(3)	87.06(19)	N(4)–Cu(2)–N(6)	84.7(2)
N(1)–Cu(1)–I(1)/O(1)	163.50(15)/160.8(3)	N(4)–Cu(2)–O(3)	167.98(18)
N(1)–Cu(1)–O(2)	91.17(19)	N(4)–Cu(2)–O(4)	101.36(18)
N(2)–Cu(1)–N(3)	87.5(2)	N(5)–Cu(2)–N(6)	87.08(19)
N(2)–Cu(1)–I(1)/O(1)	94.17(15) /96.5(3)	N(5)–Cu(2)–O(3)	103.35(18)
N(2)–Cu(1)–O(2)	173.8(2)	N(5)–Cu(2)–O(4)	169.12(19)
N(3)–Cu(1)–I(1)/O(1)	108.73(14)/111.7(3)	N(6)–Cu(2)–O(3)	98.27(18)
N(3)–Cu(1)–O(2)	89.48(18)	N(6)–Cu(2)–O(4)	98.50(17)
I(1)/O(1)–Cu(1)–O(2)	91.85(14)/89.6(3)	O(3)–Cu(2)–O(4)	66.72(16)
τ [Cu(1)]	0.172(4)/0.217(6)	τ [Cu(2)]	0.019(4)

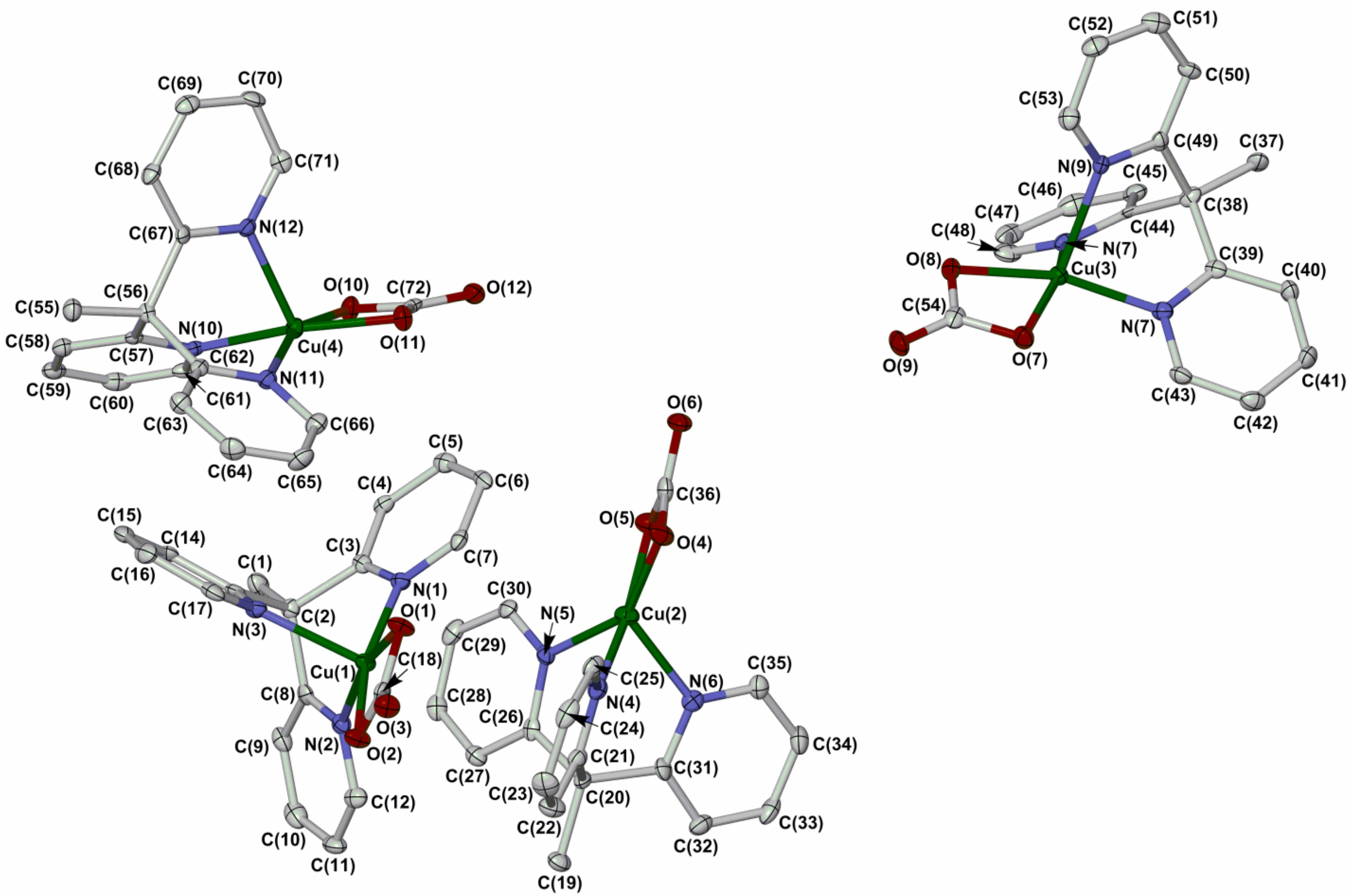

Figure S7 The four unique complex molecules in **8**·4.25H_2O, showing the atom numbering scheme employed. Displacement ellipsoids are drawn at the 50 % probability level.

Colour code: C, white; H, pale grey; Cu, green; N, blue; O, red.

Table S5 Selected bond distances and angles in the crystal structure of **8**·4.25H_2O (Å, º). See Fig. S7 for the atom numbering scheme.

Cu(1)–N(1)	1.981(3)	Cu(3)–N(7)	1.978(4)
Cu(1)–N(2)	1.975(4)	Cu(3)–N(8)	2.012(3)
Cu(1)–N(3)	2.195(4)	Cu(3)–N(9)	2.176(3)
Cu(1)–O(1)	1.968(3)	Cu(3)–O(7)	1.988(3)
Cu(1)–O(2)	1.945(3)	Cu(3)–O(8)	1.965(3)
Cu(2)–N(4)	1.971(3)	Cu(4)–N(10)	1.982(3)
Cu(2)–N(5)	2.045(3)	Cu(4)–N(11)	1.990(3)
Cu(2)–N(6)	2.139(4)	Cu(4)–N(12)	2.180(3)
Cu(2)–O(4)	1.988(3)	Cu(4)–O(10)	1.978(3)
Cu(2)–O(5)	1.956(3)	Cu(4)–O(11)	1.972(3)
N(1)–Cu(1)–N(2)	90.09(14)	N(7)–Cu(3)–N(8)	89.66(14)
N(1)–Cu(1)–N(3)	84.70(13)	N(7)–Cu(3)–N(9)	88.68(13)
N(1)–Cu(1)–O(1)	100.93(13)	N(7)–Cu(3)–O(7)	99.01(13)
N(1)–Cu(1)–O(2)	164.36(13)	N(7)–Cu(3)–O(8)	163.56(13)
N(2)–Cu(1)–N(3)	87.92(14)	N(8)–Cu(3)–N(9)	83.99(13)
N(2)–Cu(1)–O(1)	164.31(13)	N(8)–Cu(3)–O(7)	155.95(13)
N(2)–Cu(1)–O(2)	99.15(13)	N(8)–Cu(3)–O(8)	100.12(14)
N(3)–Cu(1)–O(1)	104.07(13)	N(9)–Cu(3)–O(7)	118.37(13)
N(3)–Cu(1)–O(2)	108.07(13)	N(9)–Cu(3)–O(8)	105.35(12)
O(1)–Cu(1)–O(2)	67.76(12)	O(7)–Cu(3)–O(8)	67.00(12)
N(4)–Cu(2)–N(5)	90.13(14)	N(10)–Cu(4)–N(11)	89.22(14)
N(4)–Cu(2)–N(6)	87.90(14)	N(10)–Cu(4)–N(12)	86.24(13)
N(4)–Cu(2)–O(4)	98.68(13)	N(10)–Cu(4)–O(10)	101.11(13)
N(4)–Cu(2)–O(5)	164.03(14)	N(10)–Cu(4)–O(11)	166.00(13)
N(5)–Cu(2)–N(6)	83.82(13)	N(11)–Cu(4)–N(12)	87.23(13)
N(5)–Cu(2)–O(4)	147.52(13)	N(11)–Cu(4)–O(10)	157.84(13)
N(5)–Cu(2)–O(5)	98.55(13)	N(11)–Cu(4)–O(11)	99.75(13)
N(6)–Cu(2)–O(4)	127.44(13)	N(12)–Cu(4)–O(10)	112.76(12)
N(6)–Cu(2)–O(5)	106.26(13)	N(12)–Cu(4)–O(11)	104.79(13)
O(4)–Cu(2)–O(5)	67.00(12)	O(10)–Cu(4)–O(11)	66.89(12)
τ [Cu(1)]	0.001(3)	τ [Cu(3)]	0.127(3)
τ [Cu(2)]	0.275(3)	τ [Cu(4)]	0.136(3)

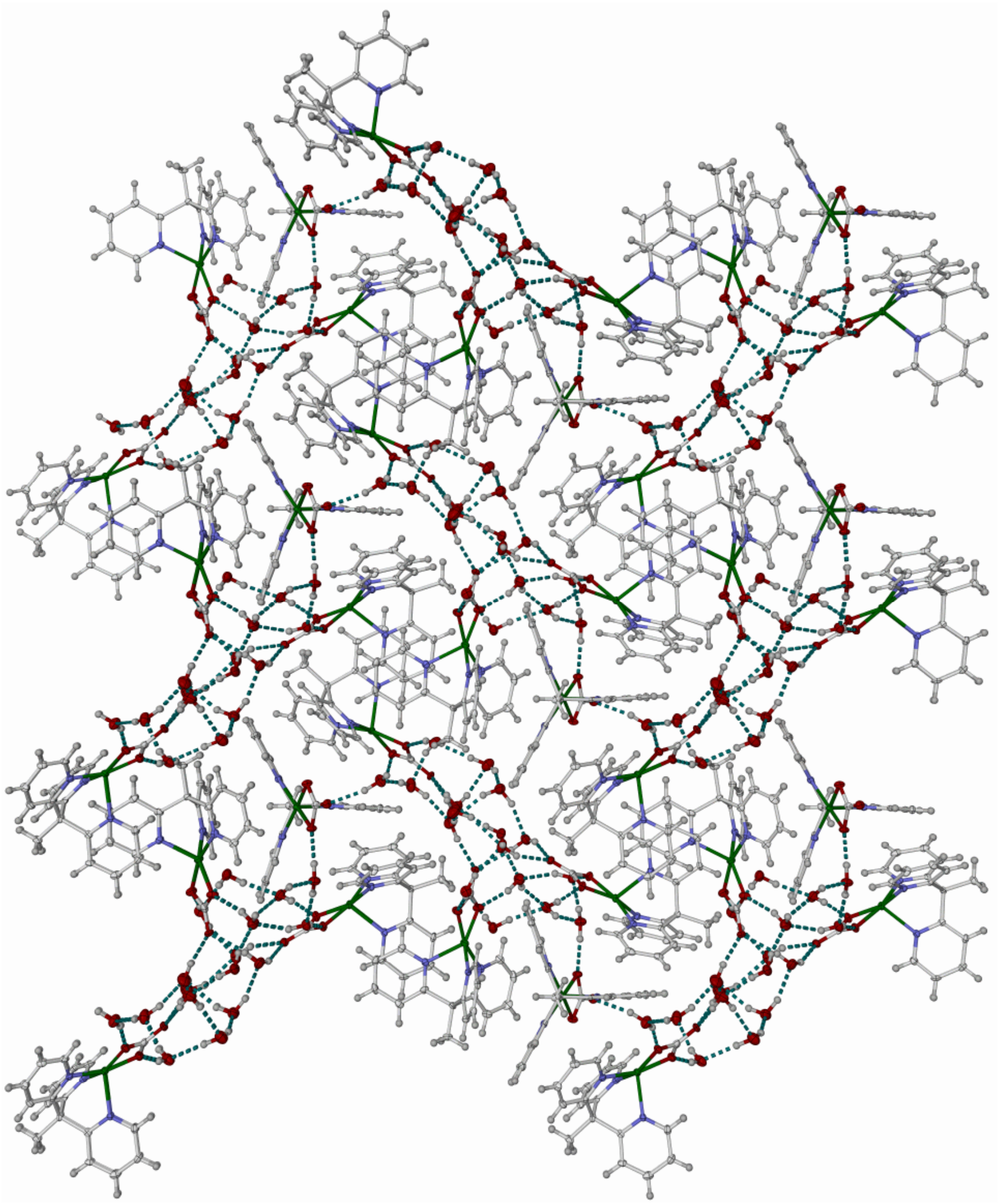

Figure S8 Packing diagram of **8**·4.25H_2O, showing the hydrogen bonding in the lattice. The view is along the [100] crystallographic vector, with *b* horizontal.

Colour code: C, white; H, pale grey; Cu, green; N, blue; O, red.

The hydrogen bonding topology in each water channel is shown more clearly in Fig. 6 of the main article.

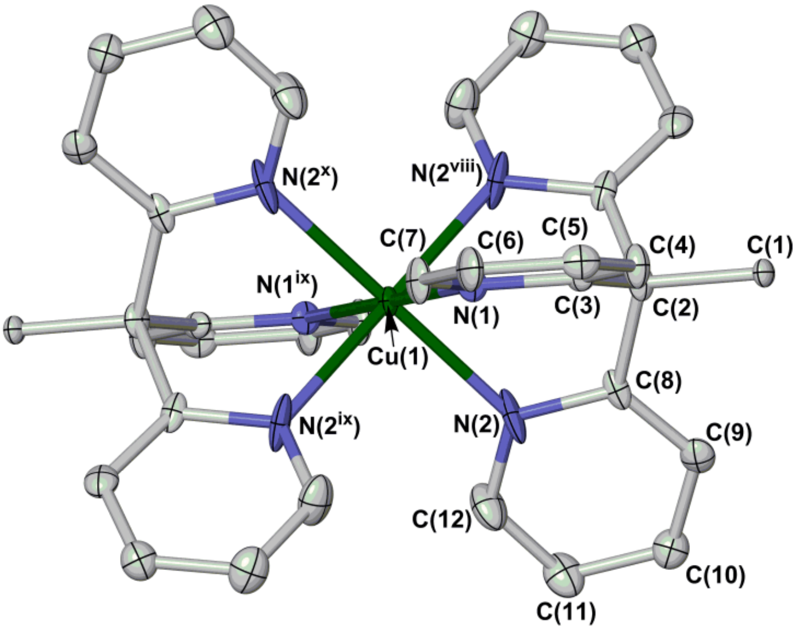

Figure S9 View of the [CuL_2]$^{2+}$ dication in the crystal structure of **9**·8H_2O. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms have been omitted for clarity. Symmetry codes: (viii) *x*, 1–*y*, *z*; (ix) 1–*x*, *y*, 2–*z*; (x) 1–*x*, 1–*y*, 2–*z*.

Colour code: C, white; Cu, green; N, blue.

Table S6 Selected bond distances and angles in the crystal structure of **9**·8H_2O (Å, º). See Fig. S## for the atom numbering scheme employed. The numbers in square brackets are ΔMSDA values <d^2> (10^4 Å^2).

Cu(1)–N(1)	1.995(5) [0.002(3)]	Cu(1)–N(2)	2.166(5) [0.027(3)]
N(1)–Cu(1)–N(1^{xi})	180	N(2)–Cu(1)–N(2^{vii})	85.7(3)
N(1)–Cu(1)–N(2)	85.17(16)	N(2)–Cu(1)–N(2^{ix})	94.3(3)
N(1)–Cu(1)–N(2^{ix})	94.83(16)	N(2)–Cu(1)–N(2^{x})	180

<d^2> is a measure of the degree of atomic libration along each bond in the molecule. A higher-than-normal value of <d^2> is indicative of unresolved disorder involving that bond.[1]

In this case, <d^2> is zero within experimental error for Cu(1)–N(1), but is significantly higher for Cu(1)–N(2). That suggests the presence of a statically or dynamically disordered Jahn-Teller elongation, distributed between the N(2)–Cu(1)–N(2^{x}) and N(2^{viii})–Cu(1)–N(2^{ix}) vectors.[2] That is also consistent with the elongated displacement ellipsoids for N(2) and its symmetry equivalents.

[1] L. R. Falvello, *J. Chem. Soc., Dalton Trans.* 1997, 4463.
[2] M. A. Halcrow, *Dalton Trans.* 2003, 4375;
M. A. Halcrow, *Chem. Soc. Rev.* 2013, **42**, 1784.

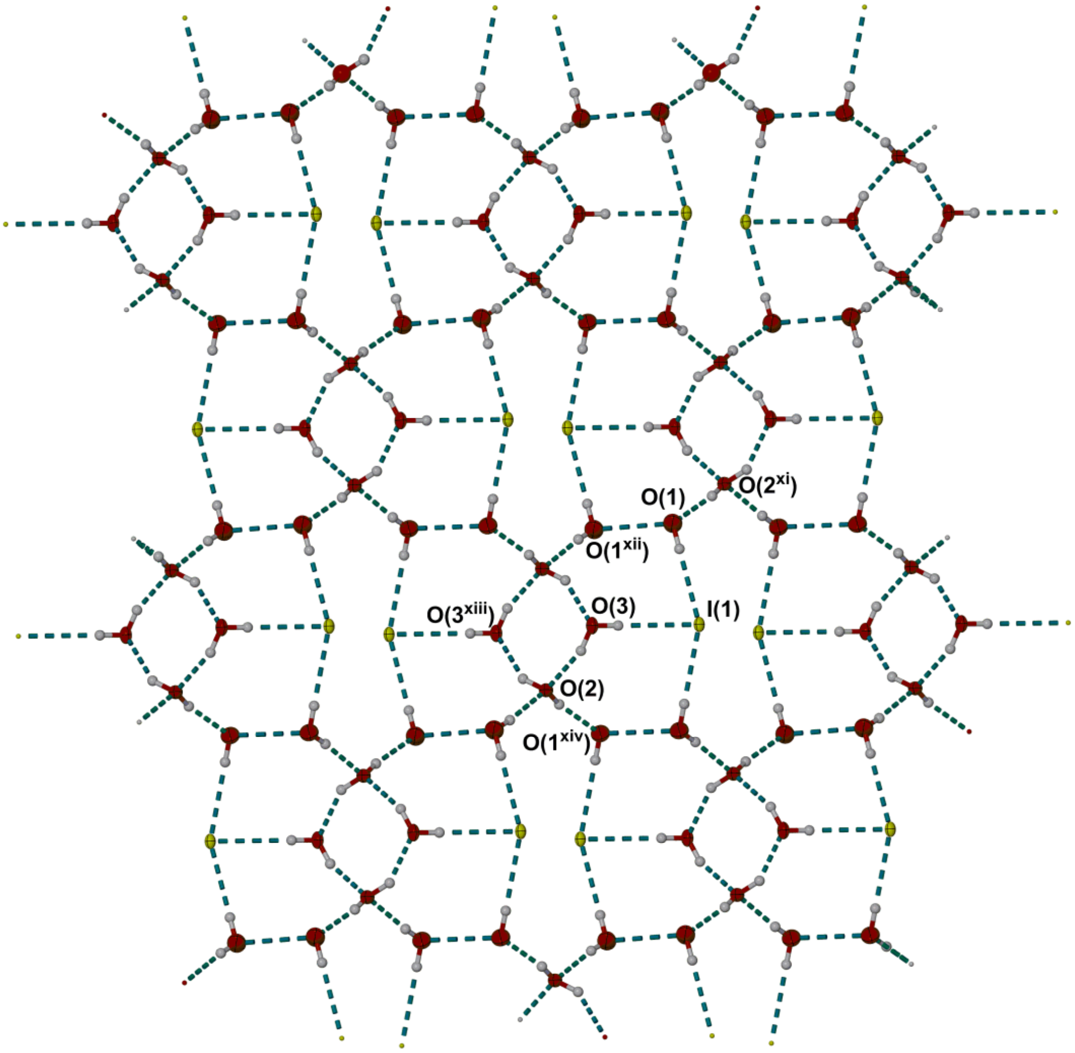

Figure S10 View of the hydrogen bonding topology in **9**·8H_2O (see also Fig. 7 of the main article). The H atoms on O(1), O(2) and O(3) all suffer from symmetry-imposed disorder, and only one orientation of the H atom array is shown. Displacement ellipsoids are drawn at the 50 % probability level. Symmetry codes: (xi) ½+*x*, ½+*y*, *z*; (xii) $^3/_2$–*x*, $^3/_2$–*y*, 1–*z*; (xiii) 1–*x*, *y*, 1–*z*; (xiv) $^3/_2$–*x*, –½+*y*, *z*.

Colour code: H, pale grey; I, yellow; O, red.

This network has a L4(6)5(6)8(10) topology, according to Infantes and Motherwell's notation.[3]

[3] L. Infantes and S. Motherwell, *CrystEngComm* 2002, **4**, 454;
L. Infantes, J. Chisholm and S. Motherwell, *CrystEngComm* 2003, **5**, 480.

Table S7 Hydrogen bond parameters for the crystal structures in this work (Å, °). See Fig. 6 (main article), Fig. S3 and Fig. S10 for the atom numbering schemes employed.[a]

	D–H	H…A	D…A	D–H…A
3·H_2O				
O(13)–H(13B)...O(4)	0.88(5)	2.11(5)	2.988(3)	172(4)
O(13)–H(13A)...O(5)	0.89(5)	1.94(5)	2.806(3)	164(4)
8·4.5H_2O				
O(13)–H(13B)...O(3^{iii})	0.899(19)	1.93(2)	2.814(5)	168(5)
O(13)–H(13A)...O(7^{iv})	0.888(19)	1.96(3)	2.818(4)	161(5)
O(14)–H(14A)...O(16)	0.903(19)	1.97(3)	2.846(5)	163(5)
O(14)–H(14B)...O(17)	0.903(19)	1.892(19)	2.793(5)	176(5)
O(15)–H(15A)...O(13)	0.908(19)	1.83(2)	2.737(5)	175(6)
O(15)–H(15B)...O(21)	0.912(19)	1.91(2)	2.801(5)	165(5)
O(16)–H(16B)...O(21)	0.901(19)	2.04(3)	2.882(6)	155(5)
O(16)–H(16A)...O(22)	0.912(19)	1.94(3)	2.806(5)	157(5)
O(17)–H(17A)...O(8)	0.886(19)	1.91(2)	2.787(4)	169(5)
O(17)–H(17B)...O(15)	0.891(19)	1.91(3)	2.757(5)	159(5)
O(18)–H(18A)...O(9)	0.91(2)	1.86(2)	2.759(5)	168(5)
O(18)–H(18B)...O(14)	0.916(19)	1.98(2)	2.878(5)	167(4)
O(19)–H(19E)...O(5)	0.883(19)	1.97(2)	2.837(4)	167(5)
O(19)–H(19D)...O(20)	0.880(19)	1.97(2)	2.833(5)	166(5)
O(20)–H(20A)...O(12)	0.899(19)	2.01(3)	2.835(5)	152(5)
O(20)–H(20B)...O(25^{iv})	0.897(19)	1.82(2)	2.696(5)	165(5)
O(21)–H(21A)...O(6)	0.909(19)	1.87(2)	2.768(5)	169(6)
O(21)–H(21B)...O(29)	0.94(2)	1.77(2)	2.685(6)	164(5)
O(22)–H(22A)...O(6)	0.882(19)	1.97(2)	2.845(5)	171(5)
O(22)–H(22B)...O(12^{i})	0.894(19)	1.91(3)	2.762(5)	158(5)
O(23)–H(23A)...O(11)	0.891(19)	1.936(19)	2.821(4)	172(4)
O(23)–H(23B)...O(24)	0.884(19)	2.15(3)	2.928(5)	147(4)
O(24)–H(24B)...O(4)	0.915(19)	1.92(2)	2.813(5)	166(5)
O(24)–H(24A)...O(27)	0.913(19)	2.17(3)	3.006(5)	152(5)
O(25)–H(25A)...O(18)	0.893(19)	1.842(19)	2.729(5)	172(4)
O(25)–H(25B)...O(24)	0.916(19)	1.88(2)	2.780(5)	166(5)
O(26)–H(26B)...O(1)	0.876(19)	1.87(2)	2.742(4)	177(5)
O(26)–H(26A)...O(23)	0.881(18)	1.912(19)	2.782(4)	169(4)
O(27)–H(27B)...O(10^{v})	0.888(19)	2.01(2)	2.891(4)	175(5)
O(27)–H(27A)...O(26)	0.899(19)	1.82(3)	2.682(5)	161(5)
O(28)–H(28B)...O(19^{v})	0.905(19)	1.93(2)	2.820(5)	169(5)
O(28)–H(28A)...O(27)	0.909(19)	1.89(2)	2.791(5)	170(5)
O(29)–H(29A)...O(9^{iv})	0.907(19)	1.87(2)	2.772(5)	173(5)
O(29)–H(29B)...O(20)	0.91(2)	2.05(3)	2.869(5)	150(5)
9·8H_2O				
O(1)–H(1D)…I(1)	0.89(2)	2.65(2)	3.540(6)	178(7)
O(1)–H(1E)…O(2^{xi})	0.88(2)	1.92(2)	2.786(6)	169(8)
O(1)…O(1^{xii})[b]	–	–	2.769(6)	–
O(2)–H(2A)…O(3^{xiii})	0.90(2)	1.96(7)	2.775(6)	150(12)
O(2)–H(2B)…O(1^{xiv})	0.90(2)	1.91(4)	2.786(6)	163(10)
O(3)–H(3A)…I(1)	0.91(2)	2.73(2)	3.636(5)	173(7)
O(3)–H(3B)…O(2)	0.90(2)	1.94(6)	2.775(6)	154(11)

[a] Symmetry codes: (iii) 1–*x*, ½+*y*, 2–*z*; (iv) –1+*x*, *y*, *z*; (v) 1+*x*, *y*, *z*; (xi) ½+*x*, ½+*y*, *z*; (xii) 3/2–*x*, 3/2–*y*, 1–*z*; (xiii) 1–*x*, *y*, 1–*z*; (xiv) 3/2–*x*, –½+*y*, *z*. [b] This hydrogen bond is implied by the H atom disorder in the structure, but no half-occupied H atom was located in the Fourier map at this position.