# A Crystalline Hydrogen-Bonded Network with a Poly-Catenate Topology

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## Electronic Supplementary Information

Supplementary Material (ESI) for Chemical Communications


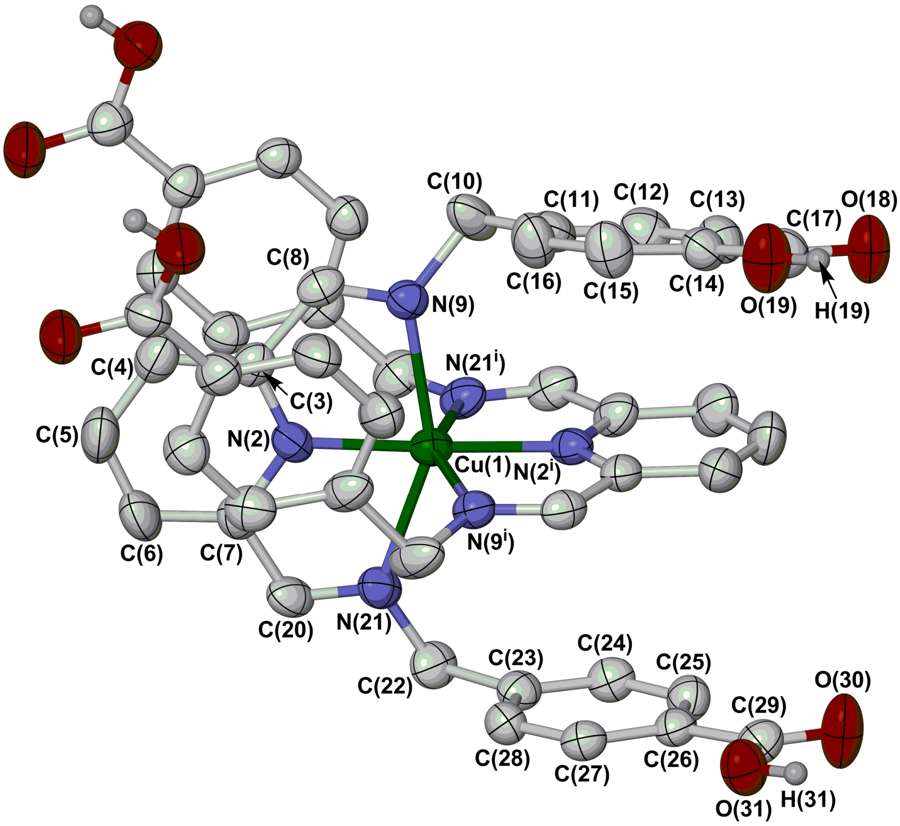


**Fig. S1** View of the complex dication in **1**·½$H_2O$, showing the full atom numbering scheme employed All C-bound H atoms have been omitted for clarity. Thermal ellipsoids are at the 50% probability level except for H atoms, which have arbitrary radii. Symmetry code (i): 1–*x*, *y*, $^{3}/_{2}$–*z*.

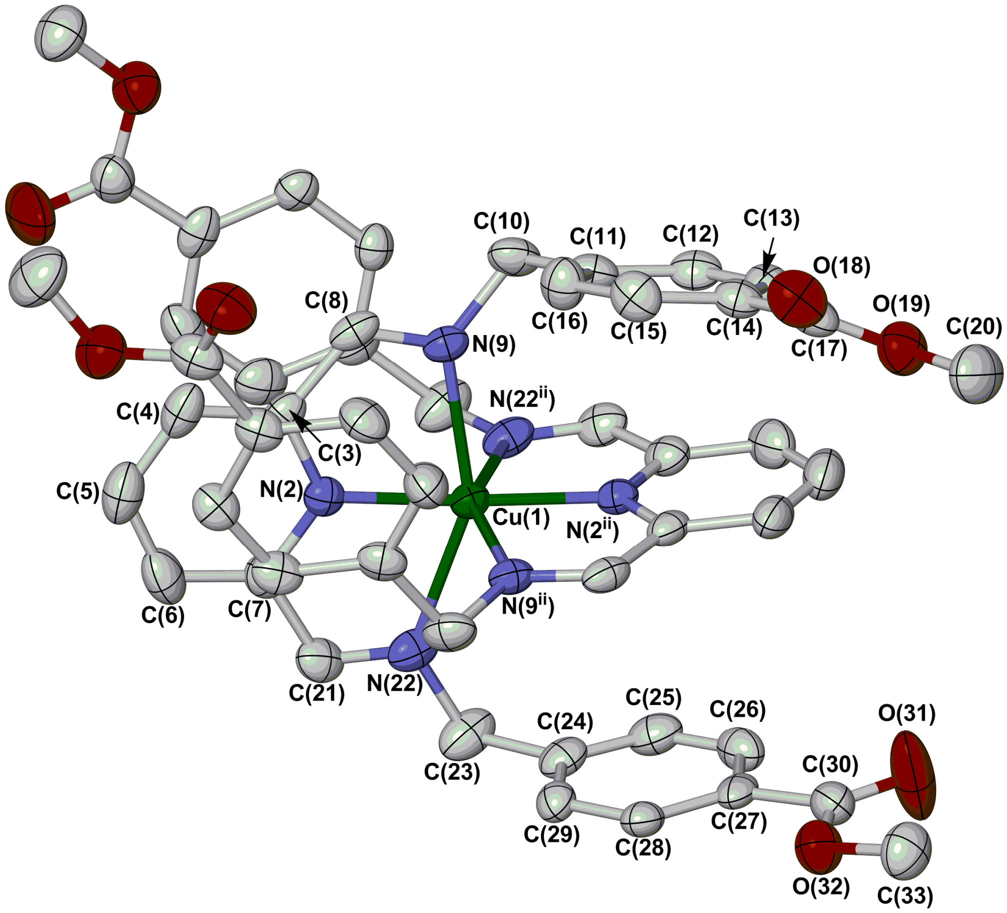


**Fig. S2** View of the complex dication in **2**·$CH_3NO_2$, showing the full atom numbering scheme employed. Details as for Fig. S1. Symmetry code (ii): –*x*, –*x*+*y*, ⅓–*z*.

**Table S1** Selected bond lengths and angles in the crystal structures in this work (Å, °).[a] Numbers in square brackets are <$d^2$> values, calculated from a TLS analysis ($10^4$ $Å^2$). See ref. 20 for more details.

| **1**·½$H_2O$ | | **2**·$CH_3NO_2$ | |
|---|---|---|---|
| Cu(1)–N(2) | 1.984(2) [13(11)] | Cu(1)–N(2) | 1.966(2) [26(10)] |
| Cu(1)–N(9) | 2.247(2) [63(12)] | Cu(1)–N(9) | 2.235(2) [11(11)] |
| Cu(1)–N(21) | 2.292(2) [50(13)] | Cu(1)–N(22) | 2.289(3) [123(13)] |
| | | | |
| N(2)–Cu(1)–N($2^i$) | 174.41(13) | N(2)–Cu(1)–N($2^{ii}$) | 171.57(11) |
| N(2)–Cu(1)–N(9) | 76.86(9) | N(2)–Cu(1)–N(9) | 77.34(9) |
| N(2)–Cu(1)–N($9^i$) | 99.35(8) | N(2)–Cu(1)–N($9^{ii}$) | 97.17(8) |
| N(2)–Cu(1)–N(21) | 76.25(9) | N(2)–Cu(1)–N(22) | 75.61(9) |
| N(2)–Cu(1)–N($21^i$) | 107.88(9) | N(2)–Cu(1)–N($22^{ii}$) | 110.42(9) |
| N(9)–Cu(1)–N($9^i$) | 96.69(12) | N(9)–Cu(1)–N($9^{ii}$) | 100.15(12) |
| N(9)–Cu(1)–N(21) | 152.47(8) | N(9)–Cu(1)–N(22) | 152.20(9) |
| N(9)–Cu(1)–N($21^i$) | 93.37(8) | N(9)–Cu(1)–N($22^{ii}$) | 89.46(8) |
| N(21)–Cu(1)–N($21^i$) | 89.33(13) | N(22)–Cu(1)–N($22^{ii}$) | 94.02(13) |

[a]Symmetry codes (i): 1–*x*, *y*, ³⁄₂–*z* ; (ii) –*x*, –*x*+*y*, ⅓–*z*.

**Table S2** Metric parameters for the hydrogen bonds in **1**·½$H_2O$ (Å, °).[a] Potential hydrogen bonding contacts involving partial water molecule O(37) are also given. Note that the placement of the carboxylic acid H atoms on O(19) and O(31) is arbitrary, and in practise these H atoms are likely to be disordered over the two O atoms in each carboxy group.

| | O–H | H...A | O...A | O–H...A |
|---|---|---|---|---|
| O(19)–H(19)…O($30^{iii}$) | 0.84 | 1.83 | 2.648(4) | 169.2 |
| O(31)–H(31)…O($18^{iii}$) | 0.84 | 1.80 | 2.617(3) | 165.6 |
| C(4)–H(4)…O($37^i$) | 0.95 | 2.27 | 3.204(10) | 167.5 |
| | | | | |
| O(37)…O(30) | | | 3.122(10) | |
| O(37)…O(31) | | | 3.397(10) | |
| O(37)...F(35B)/F(36B)/F(36C)[b] | | | 3.02(2)/3.267(18)/3.07(2) | |
| O(37)...F($35A^{iii}$)/F($34C^{iii}$)/F($36C^{iii}$)[c] | | | 2.886(11)/3.04(3)/3.25(2) | |

[a]Symmetry codes: (i): 1–*x*, *y*, ³⁄₂–*z*; (iii) ½–*x*, ½–*y*, 1–*z*. [b]The short contact O(37)…F(35A) = 2.505(12) Å implies that O(37) and disorder site 'A' of this anion cannot be simultaneously occupied. [c]The short contact O(37)…F($35B^{iii}$) = 2.349(17) Å implies that O(37) and disorder site 'B' of this symmetry-related anion cannot be simultaneously occupied.

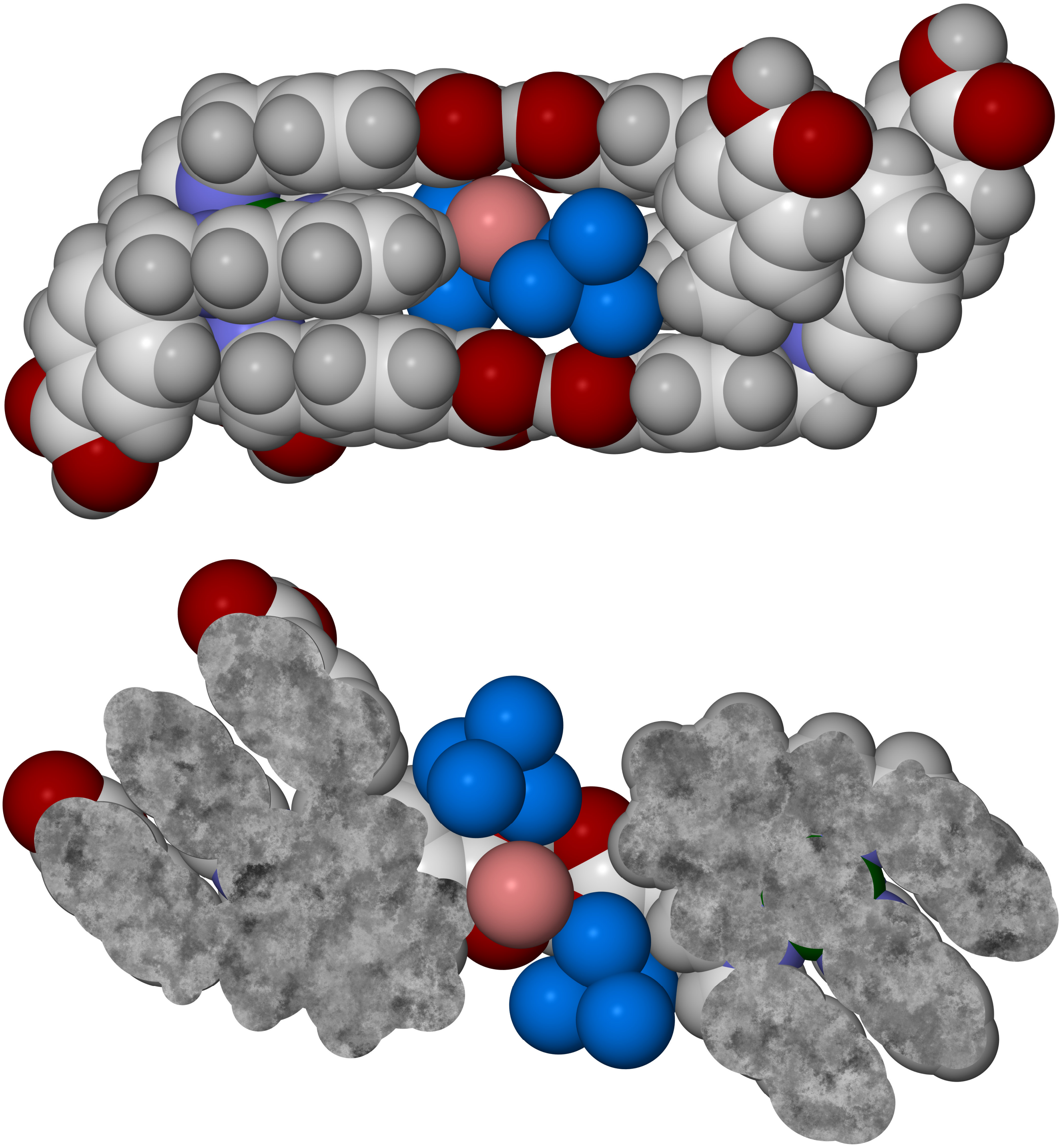

**Fig. S3** Space-filling views showing the occupancy of the ring cavities in **1**·½$H_2O$ by the $BF_4^-$ anions and partially occupied water molecule. Only one of the two symmetry-related partial water sites in the cavity, and one orientation of the disordered anions, are shown. Hydrogen atoms from the partial water site were not included in the structure refinement, and are also not shown. Top: side-on view into a cavity. Bottom: cutaway view through the top of a cavity. Colour code: C, white; H, grey; Cu, green; F, cyan; N, blue; O, red; partial water O atom, pale red.

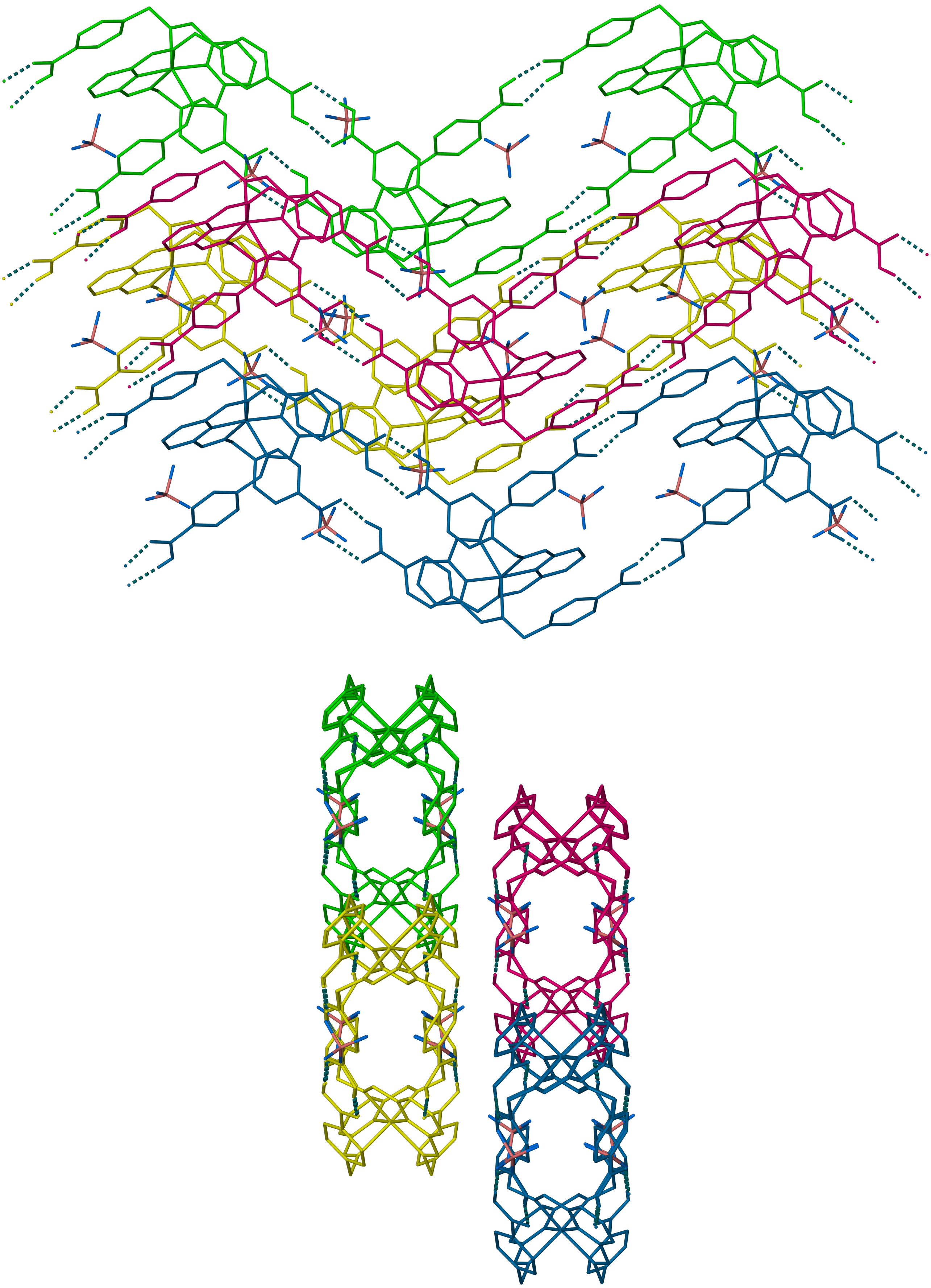

**Fig. S4** Views showing the co-parallel packing of non-interpenetrating [∞]-catenate chains in **1**·½$H_2O$, looking approximately perpendicular (top) and parallel (bottom) to the chains. Four separate chains with yellow, green, blue and magenta colouration are shown. The $BF_4^-$ anions anions are also shown (B, pink; F, cyan), but the partial water sites have been omitted for clarity.

**Table S3** *X*-band EPR data for the compounds in this work.

| | $T$ (K) | Lineshape | $g_{\parallel}$ | $g_{\perp}$ | $A_{\parallel}\{^{63,65}Cu\}$ (G) |
|---|---|---|---|---|---|
| **1**·½$H_2O$, powder | 297 | Isotropic | – | 2.16 | – |
| **1**·½$H_2O$, powder | 113 | Axial | 2.27 | 2.14 | 123 |
| | | | | | |
| **2**, powder | 297 | Axial | 2.26 | 2.15 | 118 |
| **2**, powder | 114 | Axial | 2.26 | 2.13 | 123 |
| **2**, MeCN solution[a] | 134 | Axial | 2.26 | 2.12 | 132 |
| | | | | | |
| **3**, powder[b] | 297 | "Inverse" axial | 2.06 | 2.17 | – |
| **3**, powder | 120 | Axial | 2.28 | 2.14 | 122 |

[a]Sample run in 10:1 MeCN :toluene. [b]The different lineshape of this spectrum, compared to **1**·½$H_2O$, probably simply reflects a narrower linewidth in **3** that allows the $g_3$ feature to be resolved. The inverse axial lineshape is characteristic of a copper(II) compound showing disorder of its Jahn-Teller distortion at that temperature.

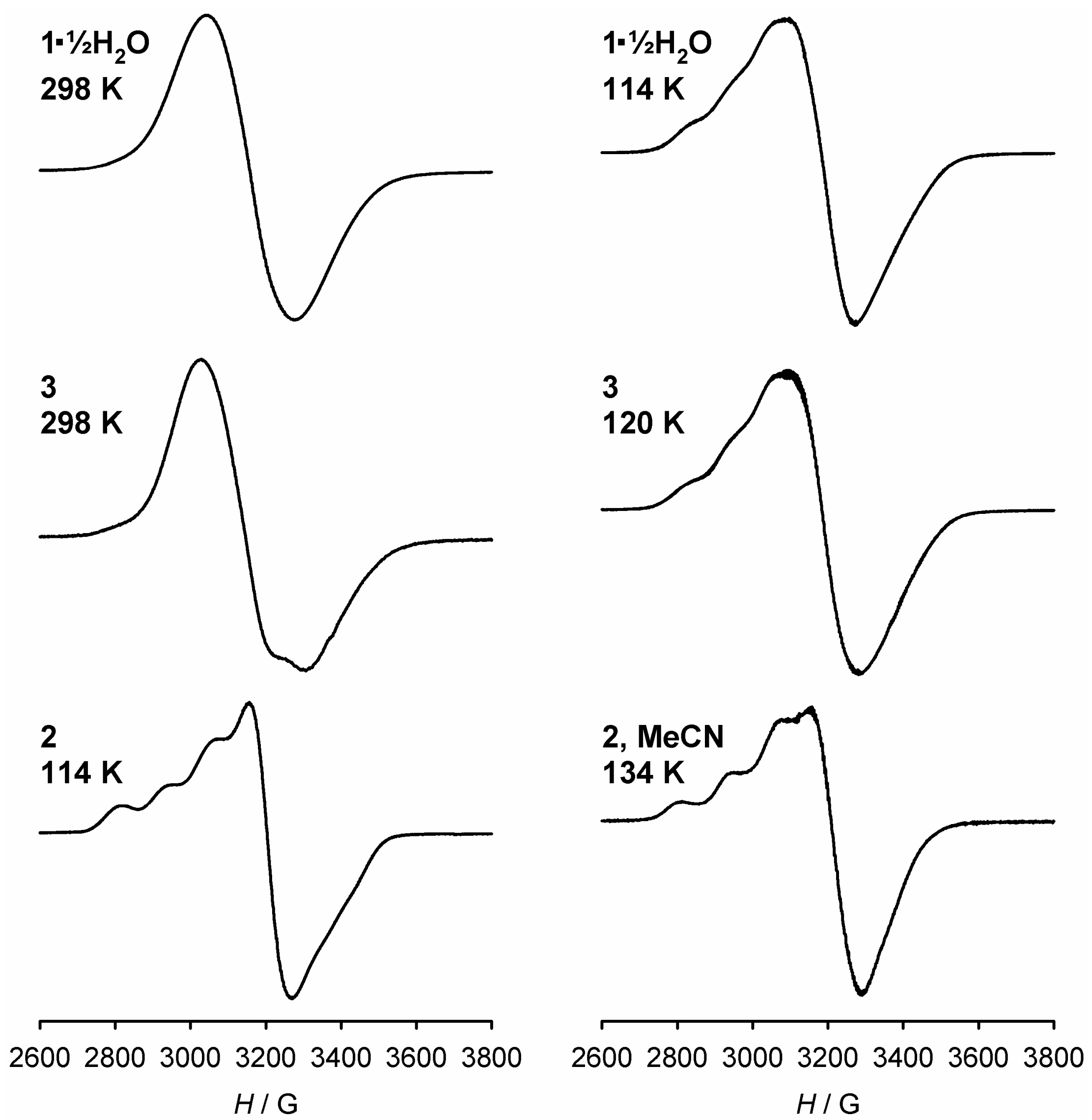


**Fig. S5** *X*-band EPR spectra of the compounds in this work in the powder and (for **2**) solution phases. $g$ and $A$ parameters are tabulated above.

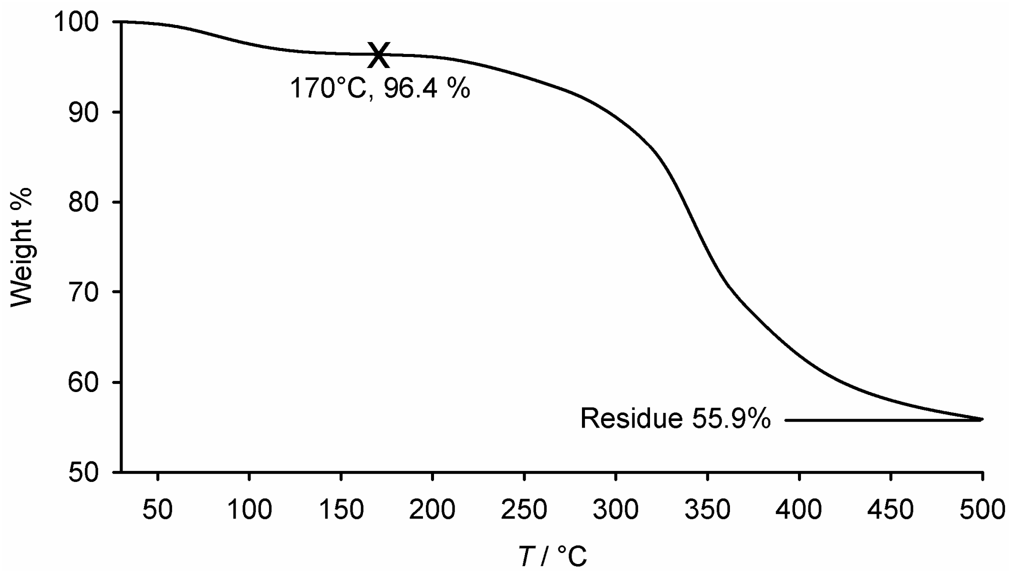


**Figure S6** Thermogravimetric analysis of **1**.

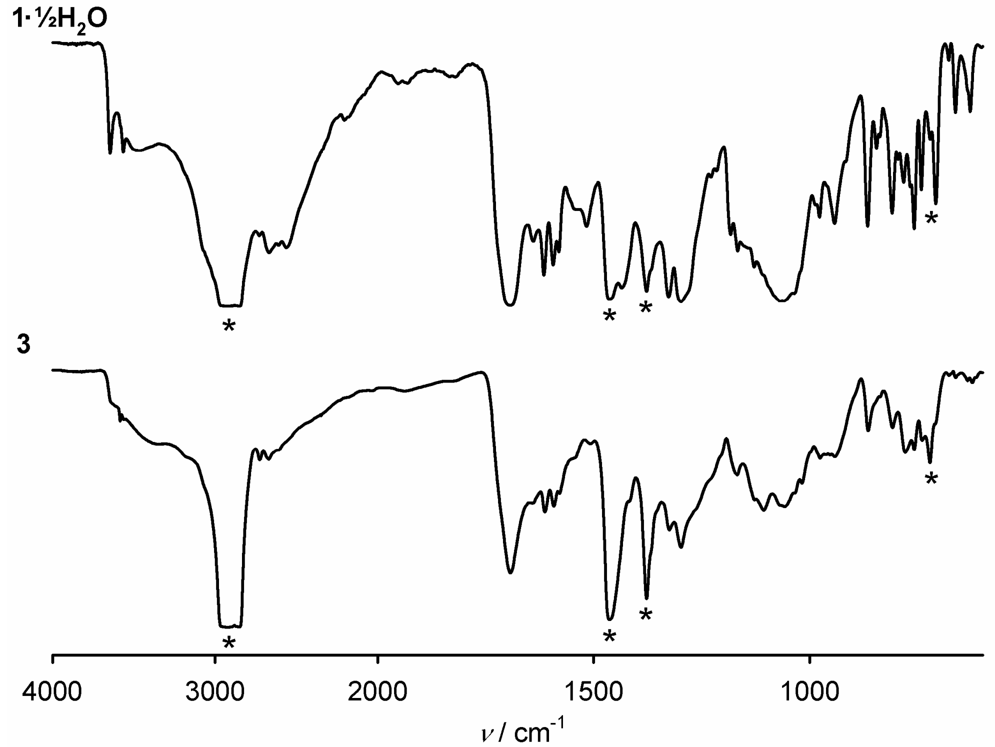


**Figure S7** Nujol mull IR spectra of **1**·½$H_2O$ and **3**. The starred peaks are from the nujol matrix.

Three sets of peaks in the spectrum of **1**·½$H_2O$ are missing in that of **3**, which can all be attributed to a water molecule in a restricted solid lattice environment (refs. below):

3565 and 3645 $cm^{-1}$: $\nu_{sym}$ and $\nu_{asym}$\{O–H\}

1516 $cm^{-1}$ (br): δ\{H–O–H\}

629 and 663 $cm^{-1}$: librational modes (rotational oscillations restricted by the lattice).

Although the spectrum of **3** is broader and weaker, all other peak maxima appear at identical wavenumbers in both spectra.

K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds Part B*, 5th ed., Wiley Interscience, New York (1997) p. 54.

V. P. Tayal, B. K. Srivastava, D. P. Khandelwal and H. D. Bist, *Appl. Spectr. Rev.*, 1980, **16**, 43.