

Programmed Helicity in Self-Assembled Hydrogen-Bonded Chains of Chiral Copper(II) Complexes

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The copper(II) complexes $[\text{Cu}(\text{H}_2\text{L}^1)\text{Cl}_2]_2[\text{CuCl}_4]\cdot\text{CH}_3\text{CN}\cdot\text{H}_2\text{O}$ ($\text{HL}^1 = N$ -6-(4-hydroxyphenyl)-2-pyridylmethyl- N,N',N' -trimethylethylenediamine), $[\text{Cu}(\text{HL}^2)\text{Cl}_2]$ ($\text{HL}^2 = N$ -4-hydroxybenzylmethyl- N,N',N' -trimethylethylenediamine) and $[\text{Cu}_2(\mu\text{-L}^3)_2(\text{H}_2\text{O})(\text{ClO}_4)]\text{ClO}_4\cdot\text{H}_2\text{O}$ ($\text{HL}^3 = N$ -2-hydroxybenzylmethyl- N,N',N' -trimethylethylenediamine) were prepared and characterised in acetonitrile solution (by ESI-MS, EPR and UV/Vis-NIR spectroscopy) and in the solid state (by

X-ray crystallography). Each copper(II) complex is chiral and has a potential inter-complex hydrogen-bond donor group. Upon crystallisation, all three copper(II) complexes undergo spontaneous enantioselective self-assembly into hydrogen-bond-linked helices.

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Introduction

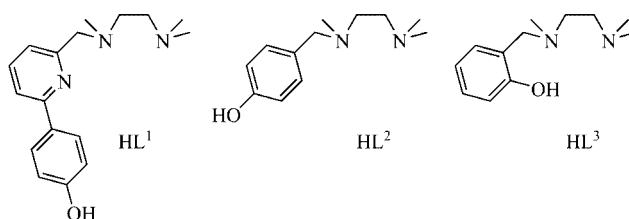
Self-assembly into spiral structures is inherent in nature, from the grandest scale – e.g. spiral galaxies^[1] – through everyday structures – e.g. the aesthetically pleasing spiral seashell – to the molecular scale – e.g. the structures of biological macromolecules such as proteins^[2] and nucleic acids.^[3] The self-organisation of the latter molecules into specific structures is, of course, vital to their function and so to all life, and has inspired the recent interest into molecules that aggregate into regular spiral topologies.^[4–8] Metal coordination complexes proffer a vast array of useful catalytic, magnetic and optical properties and so, not surprisingly, helical coordination polymers are synthetic targets for emergent applications in asymmetric catalyses, in enantioselective separations and as magnetic/optical materials.^[7,8] The design and construction of coordination polymers with helical topologies thus presents a contemporary challenge that spans coordination, supramolecular and materials chemistry.

In the majority of those helical coordination polymers reported in the literature, ditopic ligands are employed to bridge and link two adjacent metal centres.^[7,8] Herein, we demonstrate that molecular helicity can be predictably programmed into the solid-state structures of simple copper(II) coordination complexes by judicious introduction of molecular chirality through ligand design in combination with a noncovalent recognition element that induces aggregation and hence self-organisation into a spiral arrangement upon crystallisation. The natures of the new complex species in

solution were also investigated by the use of a combination of electrospray ionisation mass, UV/Visible-NIR and X-band EPR spectroscopy.

Results and Discussion

Three ligands HL^1 – HL^3 were targeted. All three are chiral and, although isolated as the racemate, upon coordination to a metal ion the chirality of the individual ligand molecule must transfer to the complex species thus formed. In HL^1 and HL^2 the positioning of the phenolic 4-OH groups prevents intramolecular hydrogen bonding interactions, but is ideal for inter-complex hydrogen bonding; therefore, these OH groups should act as a recognition element for inter-complex aggregation through hydrogen bonding. Thus, overall, simple metal complexes of HL^1 and HL^2 should be chiral and aggregate into strands through inter-complex hydrogen bonding. In contrast, the *ortho*-OH groups in HL^3 are ideally positioned for binding to a metal ion, because this was assumed that it would curtail the involvement of these groups in inter-complex aggregation. To test these predictions the three ligands were made, and their reactions with cupric chloride and cupric perchlorate studied.



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Supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the author.

Syntheses

The ligands HL¹–HL³ were prepared by direct reductive amination reactions of *N,N,N'*-trimethylethylenediamine with the appropriate aldehyde. For HL¹, tetrahydropyran (THP) protected 4-phenol-6-pyridylaldehyde was used and the THP protecting group was removed with pyridinium tosylate in 95% ethanol. Three crystalline materials were obtained from the reactions of the ligands with the cupric salts: A green powder was obtained from HL¹ and CuCl₂ in methanol/ether that afforded clear, gold-brown platelets of [Cu(HL)Cl₂]₂[CuCl₄]·MeCN·2H₂O upon recrystallisation from acetonitrile/methanol, green crystalline [Cu(HL²)Cl₂] deposited from solution of HL² and CuCl₂ in methanol/ether, and dark green-black [Cu₂(L³)₂(H₂O)(ClO₄)]ClO₄·H₂O crystallised from an alkaline (pH 9) aqueous solution of cupric perchlorate and HL³.

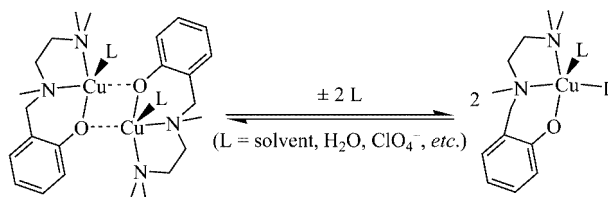
Solution Physicochemical Properties

Positive-mode ESI-MS, X-band EPR (at 77 K) and UV/Vis-NIR spectra were acquired to give information about the species in acetonitrile solutions; the data are listed in the Experimental Section and spectra are shown in the supporting information, Figure S1 and Figure S2 (for supporting information see also the footnote on the first page of this article). The ESI-MS spectrum of [Cu(H₂L¹)Cl₂]₂·[CuCl₄] shows only peaks for the [Cu(H₂L¹)Cl₂]⁺ ion (at *m/z* 419; calcd. *m/z* 419.06) suggesting that this is the only cationic species in solution. The EPR spectrum of the frozen acetonitrile solution at 77 K reveals overlaid axial sub-spectra for two nonequivalent copper(II) centres, a four/five-coordinate tetragonally distorted ion [*g*_{||} ≈ 2.26 (*A*_{||} ≈ 156 G) >> *g*_⊥ ≈ 2.07] and a distorted tetrahedral species [*g*_{||} ≈ 2.39 (*A*_{||} ≈ 120 G) >> *g*_⊥ ≈ 2.09], which is attributed to [CuCl₃(MeCN)_x][−] (in acetonitrile solution, [CuCl₄]^{2−} is only observed at high chloride concentrations^[11]). The UV/Vis-NIR spectrum shows a broad asymmetric band at 676 nm with a long low-energy tail, distinctive for a tetragonally distorted ion; the lowest energy transition for [CuCl₃(MeCN)_x][−] is reported at 405 nm and is hidden in the intense UV tail.^[11]

The ESI-MS spectrum of [Cu(HL²)Cl₂] was very weak until 1% acetic acid was added to the carrier solvent; in the presence of the acetic acid, [Cu(HL²)Cl]⁺ (at *m/z* 306; calcd. *m/z* 306.06) was observed along with peaks for the protonated ligand, (H₂L²)⁺, and ions that result from chloride–acetate exchange. The results are consistent with [Cu(HL²)Cl₂] persisting into acetonitrile solution. The EPR spectrum of the complex in acetonitrile solution at 77 K is axial and thus indicative for a tetragonally-distorted species with a *d*_{x²−y²} ground-state and the UV/Vis-NIR spectrum shows a broad asymmetric visible band at 676 nm with distinct tail to low energy (identically with [Cu(H₂L¹)Cl₂]⁺); these spectra are consistent with [Cu(HL²)Cl₂] dissolving unchanged in acetonitrile.

The main peak in the ESI-MS spectrum of [Cu₂(L³)₂·(H₂O)](ClO₄)₂ at *m/z* 270 corresponds to the monomeric

species [Cu(L³)]⁺ (calcd. *m/z* 270.08). The solid complex is EPR silent indicative for antiferromagnetic coupling between the two copper(II) centres relayed by the phenolate bridges in the dimeric [Cu₂(L³)₂(H₂O)]²⁺ cation. The EPR spectrum of a frozen acetonitrile solution of the complex at 77 K shows a strong axial signal [*g*_{||} = 2.25 (*A*_{||} = 165 G) >> *g*_⊥ = 2.06] for a tetragonal monomer suggesting that the dimer dissociates in solution according to:



The UV/Vis-NIR spectrum differs from those of the other two complexes: It shows a relatively sharp and intense σ-phenolate → Cu^{II} charge-transfer band at 430 nm^[12,13] plus a weaker visible (*d-d*) band at 625 nm; these two bands are blue shifted by ca. 30 and 85 nm, respectively, as a 1:1 EtOH/water solution is made alkaline (pH raised from 7 to 10). The EPR and UV/Vis-NIR spectra are very similar to those of other copper(II) dimers of chelating ligands with a phenolate sidearm that break up in donor solvents to monomeric species.^[12,13]

Crystal Structures

[Cu(HL)Cl₂]₂[CuCl₄]·CH₃CN·2H₂O: The crystal structure confirms the identity of the complex salt as [Cu(H₂L¹)Cl₂]₂[CuCl₄]. The structure of the [Cu(H₂L¹)Cl₂]⁺ ion is illustrated in Figure 1. Immediately obvious is that the terminal tertiary amine of HL¹ is protonated and “dangling” in the [Cu(H₂L¹)Cl₂]⁺ ion. This is expected: the tertiary amine is a relatively weak donor to a metal ion due to steric effects but is strongly basic and, therefore, protonation is favoured over coordination to a metal ion under the weakly acidic conditions in solutions of simple metal salts. As it must be, the [Cu(H₂L¹)Cl₂]⁺ complex cation is chiral, with HL¹ wrapped about the copper centre, which is bound by the pyridyl and the adjacent chiral, tertiary amine donors (nitrogen atoms N1 and N2, respectively). Within the crystal, both enantiomers of [Cu(H₂L¹)Cl₂]⁺ appear and are related by crystallographic inversion; see below. The Cu–N and Cu–Cl distances in the [Cu(H₂L¹)Cl₂]⁺ ion are listed in the caption to Figure 1 and are indicative for a copper(II) centre.^[13–17] The two largest angles about the copper ion, the *transoid* angles Cl1–Cu1–N2 [132.5(2)°] and Cl2–Cu1–N1 [152.2(2)°], give β = 71.2° and ω = 51.4° [where β = 90° and ω = 0° for square-planar geometry (*D*_{4h}) and β = 54.7° and ω = 90° for tetrahedral geometry (*T*_d)], thus revealing the geometry of Cu1 is near to midway between ideal square-planar and ideal tetrahedral. The [CuCl₄]^{2−} counter-anions exhibit a much less flattened tetrahedral geometry, which is commonplace for this ion:^[14] the *transoid* equatorial angles Cl3–Cu2–Cl3* [124.3(1)°] and Cl4–Cu2–Cl4* [138.7(3)°] yield β = 60.3° and ω = 77.9°.

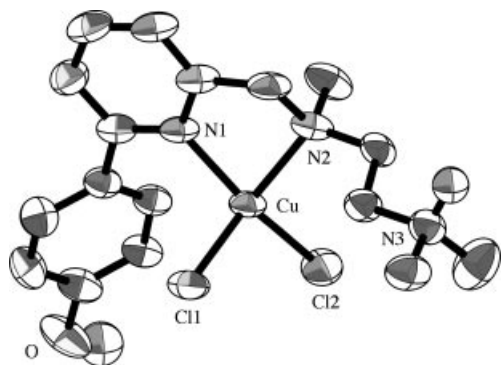


Figure 1. View of the $[\text{Cu}(\text{S-H}_2\text{L}^1)\text{Cl}_2]^+$ complex ion (50% thermal ellipsoids at 295 K are shown; hydrogen atoms on carbon are omitted for clarity). Key metric data – bond lengths [Å]: Cu1–Cl1 2.256(2), Cu2–Cl3 2.257(2), Cu1–Cl2 2.192(2), Cu2–Cl4 2.208(3), Cu1–N1 1.965(5), Cu1–N2 2.054(5); bond angles [°]: Cl1–Cu1–Cl2 101.82(7), Cl3–Cu2–Cl3* 124.3(1), Cl1–Cu1–N1 97.9(2), Cl3–Cu2–Cl4 102.2(1), Cl1–Cu1–N2 132.5(2), Cl3–Cu2–Cl4* 96.83(9), Cl2–Cu1–N1 152.2(2), Cl4–Cu2–Cl4* 138.7(3), Cl2–Cu1–N2 98.9(2), N1–Cu1–N2 81.5(2).

As predicted, homochiral $[\text{Cu}(\text{H}_2\text{L}^1)\text{Cl}_2]^+$ ions self-assemble along the y axis into helical chains that are held together by hydrogen bonding between the phenol OH group (O1) and the chloride co-ligand Cl1 ($\text{H}_{\text{O}1}\cdots\text{Cl}1$ 2.163 Å), Figure 2. The helices, in which the adjacent cations are inter-related by a 2_1 crystallographic screw, are quite open with large grooves, Figure 2 (b). The helices interweave to afford layers parallel to the yz plane, Figure 2 (c). Within a layer all cations have the same chirality and, therefore, all helices identical (M or P) handedness, but adjacent helices within the layers run in the opposite direction; the S -enantiomer, i.e. $[\text{Cu}\{(S)\text{-H}_2\text{L}^1\}\text{Cl}_2]^+$, affords the left-handed

(M) helices. The helices alternate in chirality parallel to the x -axis so adjacent layers contain cations and helices of opposite chirality. The $[\text{CuCl}_4]^{2-}$ anions are interspersed between the cation layers and each forms a $\text{Cl}\cdots\text{H}^+\cdots\text{NHR}$ hydrogen bond ($\text{Cl}3\cdots\text{N}3$ 3.290 Å) to the nearest cation in the two adjacent layers. The lattice acetonitrile and water molecules fill voids in $[\text{CuCl}_4]^{2-}$ anion layers; notably each water (W) is well-positioned to form hydrogen bonds with the nearest $[\text{Cu}(\text{H}_2\text{L}^1)\text{Cl}_2]^+$ ion ($\text{O}_\text{W}\cdots\text{Cl}2$ 3.259 Å) and the adjacent $[\text{CuCl}_4]^{2-}$ anion ($\text{O}_\text{W}\cdots\text{Cl}4$ 3.391 Å).

$[\text{Cu}(\text{HL}^2)\text{Cl}_2]$: Figure 3 presents a view of the complex molecule. The copper(II) centre is four coordinate, bound by the two amine nitrogen atoms of HL^2 and two chloride co-ligands with Cu–N and Cu–Cl distances that are typical of those of other copper(II) chloride complexes of ethylenediamine derivatives (e.g. $[\text{Cu}(\text{ethylenediamine})\text{Cl}_2]^{15}$

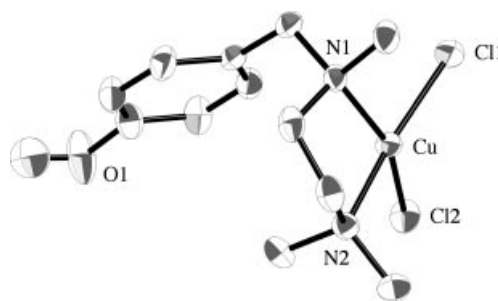


Figure 3. View of the $[\text{Cu}(\text{R-HL}^2)\text{Cl}_2]$ complex molecule (50% thermal ellipsoids at 295 K are shown; hydrogen atoms on carbon are omitted for clarity). Key metric data – bond lengths [Å]: Cu–Cl1 2.263(1), Cu–Cl2 2.269(1), Cu–N1 2.086(3), Cu–N2 2.045(3); bond angles [°]: Cl1–Cu–Cl2 93.0(1), Cl1–Cu–N1 92.9(1), Cl1–Cu–N2 171.1(1), Cl2–Cu–N1 157.7(1), Cl2–Cu–N2, 91.7(1), N1–Cu–N2 85.5(1).

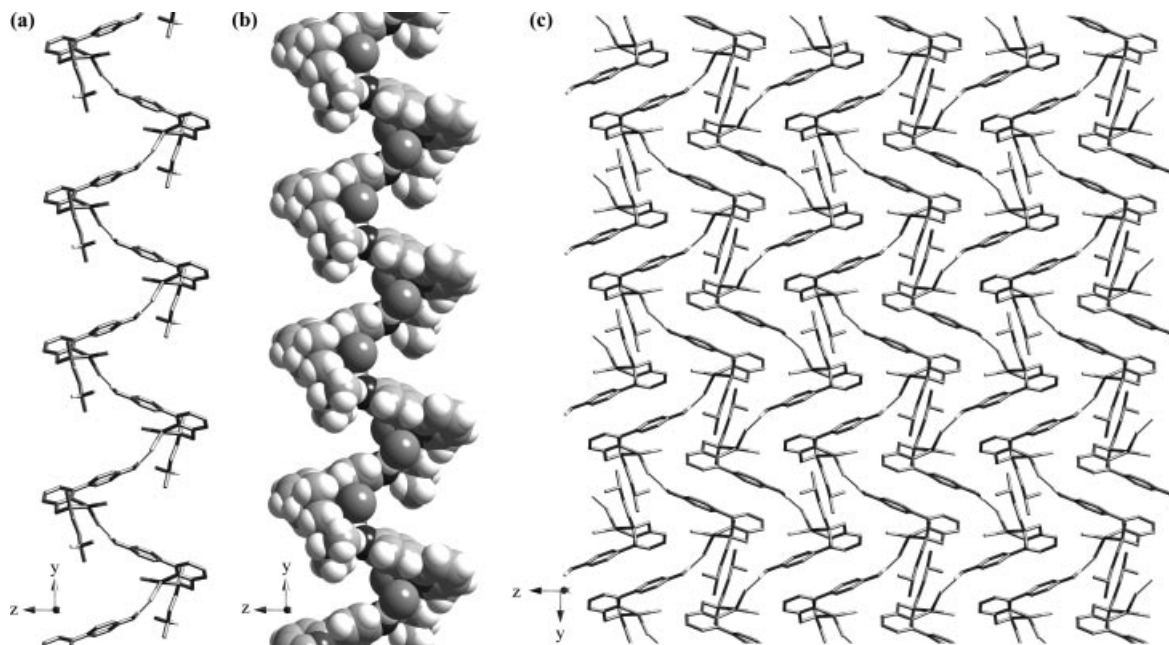


Figure 2. $[\text{Cu}(\text{H}_2\text{L}^1)\text{Cl}_2]_\infty$ helices: (a) stick view of a M -helix, (b) spacefilling view (CPK van der Waals radii) of a M -helix from the same perspective as (a); (c) view of a layer illustrating the antiparallel packing of the helices, all of which have the same (M) handedness. For clarity, those hydrogen atoms not involved in hydrogen bonding are omitted from views (a) and (c).

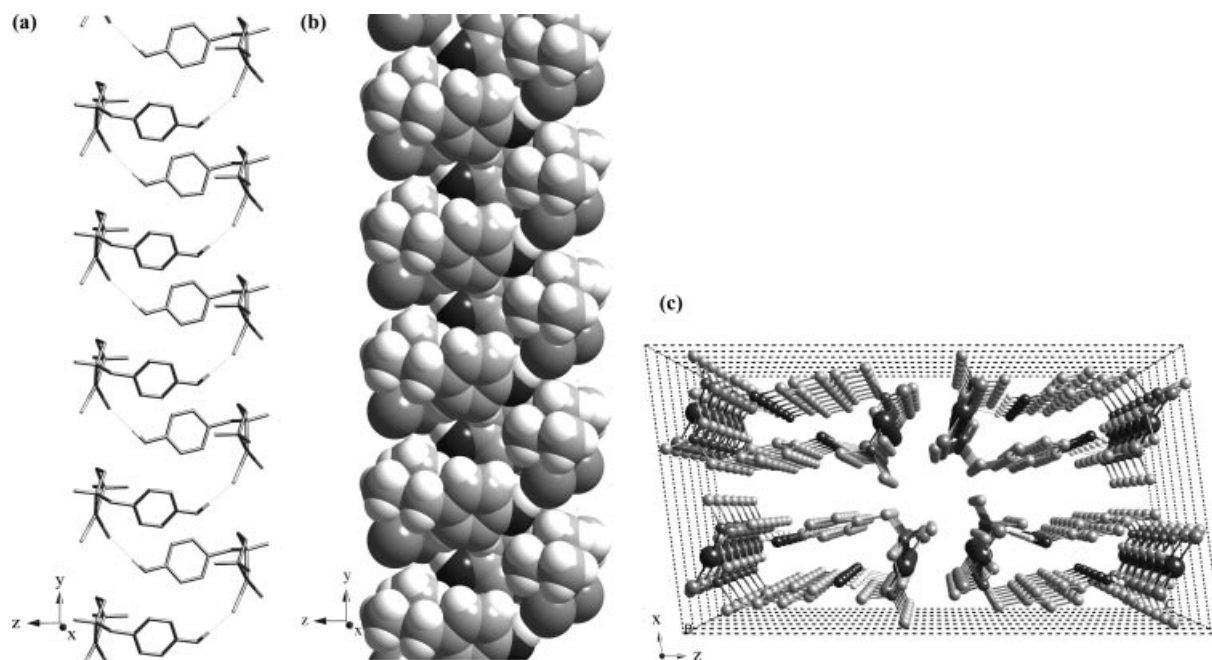


Figure 4. $[\text{Cu}(\text{HL}^2)\text{Cl}_2]_\infty$ helices: (a) view of a single *P*-helix (with carbon-bound hydrogen atoms omitted for clarity); (b) spacefilling view (CPK van der Waal's radii) showing the tight packing of complex molecules in a *P*-helix drawn from the same perspective as (a); (c) ball-and-stick perspective view of the crystal structure showing the packing of the helices of opposite chirality along the *y* axis (the top left and bottom right helices are left-handed, the others right-handed).

Cu–N 2.010 and 2.017 Å, Cu–Cl 2.286 and 2.301 Å; $[\text{Cu}(\text{trans-}N,N,N',N'\text{-tetramethylcyclohexane-1,2-diamine})\text{Cl}_2]^{[16]}$ Cu–N 2.052 Å, Cu–Cl 2.247 Å). The *transoid* angles about copper, N2–Cu–Cl1 171.1(1)° and N1–Cu–Cl2 157.7(1)°, give $\beta = 82.2^\circ$ and $\omega = 21.9^\circ$ indicative for moderate tetrahedral distortion away from square-planar geometry.

The hydroxy group of HL^2 is, as predicted, involved in intermolecular hydrogen bonding. The enantiomers of $[\text{Cu}(\text{HL}^2)\text{Cl}_2]$ separate and self-assemble into helices parallel to the *y* axis, Figure 4. Within each helix, the $[\text{Cu}(\text{HL}^2)\text{Cl}_2]$ molecules all have the same handedness and adjacent complexes are linked by hydrogen bonding between the chloride co-ligand (Cl2) on one and the hydroxy group of HL^2 on the other ($\text{Cl}\cdots\text{H}$ 2.103 Å), Figure 4(a). The crystal is the racemate in which the *P*-helices are comprised of the $[\text{Cu}(\text{R-HL}^2)\text{Cl}_2]$ enantiomer (i.e. from the *R*-enantiomer of the ligand). Comparison of the space-filling representations of the $[\text{Cu}(\text{H}_2\text{L}^1)\text{Cl}_2^+]_\infty$ helix, Figure 2 (b), and the $[\text{Cu}(\text{HL}^2)\text{Cl}_2]_\infty$ helix, Figure 4 (b), shows the grooves in the latter helices to be considerably more tightly packed and shallow. Thus, whereas the $[\text{Cu}(\text{H}_2\text{L}^1)\text{Cl}_2^+]_\infty$ helices interweave in the crystal (see Figure 2, c), each $[\text{Cu}(\text{HL}^2)\text{Cl}_2]_\infty$ helix packs largely independently of the others, Figure 4 (c); there are no significant interactions with the four nearest-neighbour helices, which have opposite chirality (because the chirality of the helices alternates along both the *x* and *z* axes).

$[\text{Cu}_2(\mu\text{-L}^3)_2(\text{H}_2\text{O})(\text{ClO}_4)]\text{ClO}_4\cdot\text{H}_2\text{O}$: The $[\text{Cu}_2(\text{L}^3)_2(\text{H}_2\text{O})(\text{ClO}_4)]^+$ cation, Figure 5, consists of two independent five-coordinate copper(II) centres, Cu1 and Cu2. Both copper ions are bound by the same enantiomer of L^3 (so the dimers are the chiral *R,R*- and *S,S*-enantiomers) and exhibit

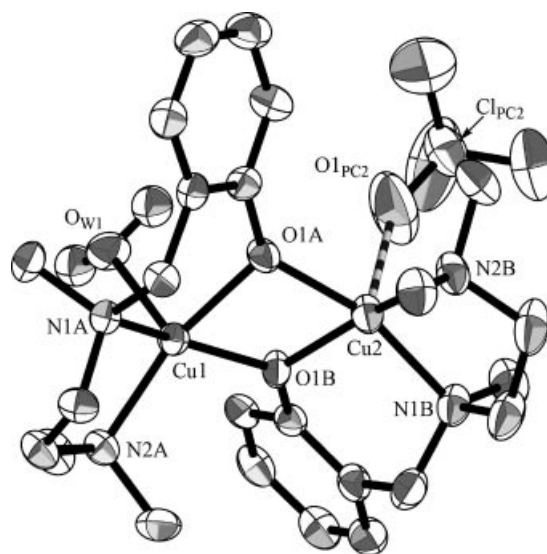


Figure 5. View of the $[\text{Cu}_2(\text{S-L}^3)_2(\text{H}_2\text{O})(\text{ClO}_4)]^+$ complex ion (50% thermal ellipsoids at 295 K are shown; W = water, PC = perchlorate). Key metric data – bond lengths [Å]: Cu1–O1A 1.987(3), Cu2–O1A 1.955(3), Cu1–N1A 2.032(4), Cu2–O1B 1.940(3), Cu1–N2A, 2.046(4), Cu2–N1B 2.023(4), Cu1–O1B 1.995(3), Cu2–N2B, 2.034(4), Cu1–OW1, 2.223(3), Cu2 $\cdots$ O1Pc2 2.580(3); bond angles [°]: O1A–Cu1–N1A 92.3(1), O1B–Cu2–N1B 92.6(1), O1A–Cu1–N2A 163.8(2), O1A–Cu2–N1B 163.1(2), O1A–Cu1–O1B 74.4(1), O1A–Cu2–O1B 76.3(1), O1A–Cu1–OW1 95.0(1), O1A–Cu2–O1Pc2 93.8(1), N1A–Cu1–N2A 86.5(2), N1B–Cu2–N2B 87.3(2), N1A–Cu1–O1B 156.4(1), O1B–Cu2–N2B 167.0(2), N1A–Cu1–OW1 101.1(2), N1B–Cu2–O1Pc2 99.1(2), N2A–Cu1–O1B 100.8(2), N2B–Cu2–O1Pc2 102.4(2), N2A–Cu1–OW1 101.1(1), O1A–Cu2–N2B 100.6(2), O1B–Cu1–OW1 99.4(1), O1B–Cu2–O1Pc2 90.5(1), Cu1–O1A–Cu2 101.2(1).

square-pyramidal geometries (trigonality indices:^[17] Cu1, $\tau = 0.12$; Cu2, $\tau = 0.07$). The two amine nitrogen atoms and the phenolate oxygen atom of L^3 are equatorially bound, and each phenolate group also bonds to the fourth equatorial position of the other copper, thereby producing a phenolate-bridged dimer with Cu1...Cu2 3.047 Å. The equatorial Cu–O/N distances at 2.00 ± 0.5 Å are indicative for copper(II).^[13–17] An axial water (W1) completes the coordination sphere of Cu1 [Cu1–O_{W1} = 2.223(3) Å] and a weakly bound, axial perchlorate [PC2: Cu2–O1_{PC2} = 2.580(3) Å] that of Cu2; the axial water and the perchlorate ligands lie to the same side of the equatorial Cu₂O₂ plane and are hydrogen-bonded to a lattice water (W2).

Given that the phenol group of L^3 becomes involved in binding to the copper(II) ions as anticipated (see above), it was a surprise to find that the homochiral [Cu₂(L^3)₂(H₂O)–

(ClO₄)]⁺ ions also self-assemble along with the (second) perchlorate counterion and a lattice water into 2₁ helices parallel to the *y* axis, Figure 6. Spiral hydrogen-bond-linked chains comprised of the axial water ligand (W1), a perchlorate (PC1), and a lattice water (W2) form the helix cores; see Figure 6 (c). The hydrogen bond lengths in the spiral [(H₂O)₂(ClO₄)]_∞ core are given in the Supporting Information (Figure S3). The dicopper(II) ions do not directly hydrogen bond with each other, but rather water W1, the axial ligand to Cu1, forms the link between each copper(II) dimer and the spiral core. The crystal is the racemate containing *M* and *P* helices; the chirality of the helices derives from the copper dimers with the *S,S*-enantiomer producing the *P*-helix (that shown in Figure 6, a–c). Figure 6 (d) illustrates the packing of the helices in the crystal. Helices of the same handedness align parallel to the *x*-axis and helices

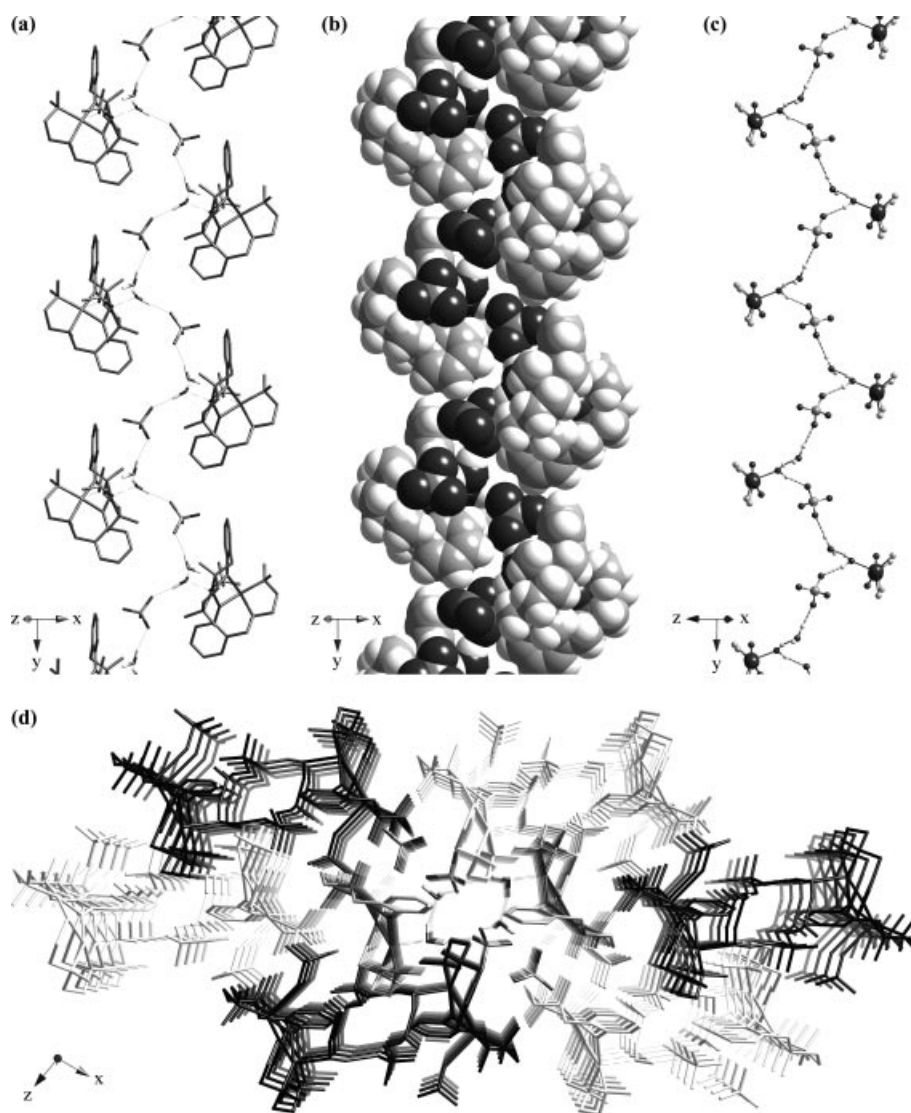


Figure 6. [Cu₂(μ - L^3)₂(H₂O)(ClO₄)](ClO₄)·(H₂O)_∞ helices: (a) view of a *P*-helix, (b) spacefilling view (CPK van der Waal's radii) of a *P*-helix from the same perspective as (a); (c) view of a *P*-helix core illustrating the spiral [(H₂O)₂(ClO₄)]_∞ chain (with carbon atoms, the hydrogen atoms attached to these and the perchlorate ligand (PC2) all omitted for clarity); (d) perspective view down a *P*-helix showing the packing of the six surrounding helices. For clarity, the neighbour helices are alternatively shaded light and dark in view (d) and those hydrogen atoms not involved in hydrogen bonding are omitted from views (a) and (d).

alternate in handedness parallel to the *z*-axis, so that each helix is surrounded by six neighbours, two of the same handedness and four of the opposite handedness.

Conclusion

Three new helical copper(II) coordination polymers have been prepared and characterised. These examples serve to demonstrate that a weak inter-ion, noncovalent recognition element, hydrogen bonds involving a phenol or water OH group within the complex species, in concert with the chiral twist of the complex cation is perfectly sufficient to cause aggregation into spirals. Zigzag chains^[7,8] of hydrogen-bonded complexes alternating in chirality were not observed in this work. In the three crystal structures, the spontaneous enantioselective self-assembly of the complexes within each helix suggests a self-recognition process must play a role in each crystallisation just as hydrogen bonding between complimentary bases dictates DNA double strand formation. Notably, the adjacent copper(II) complexes are crystallographically inter-related by a 2₁ screw. Given the weak directionality of the phenol OH...Cl–Cu or Cu–OH₂...O (H₂O or ClO₄[–]) hydrogen bonds, this is not surprising – it is the simplest possible symmetry relationship between the adjacent hydrogen-bonded complexes in a helix. Likewise, a majority of the recently reported coordination polymer helices^[7,8] align along a twofold screw axis. The obvious implication, of course, is that a recognition element(s) of greater complexity with inbuilt directionality in the non-covalent interaction – i.e. more information content – is necessary for predictable self-assembly of helices of higher symmetry.

Experimental Section

General: ¹H and ¹³C{¹H} NMR spectra were recorded at 300 K with a Bruker AC 300F spectrometer (300 MHz) operating at 300.13 MHz. Electrospray Ionisation (ESI) mass spectra were acquired with a VG Quattro mass spectrometer operating with a capillary voltage of 4 kV and a cone voltage of 30 V at 60 °C with a feed solvent of CH₃CN/water (1:1, v/v). Electronic spectra of the complexes were recorded between 220 and 2000 nm with a CARY 5 spectrometer in the dual beam mode; solution spectra were recorded in sealed 1-cm quartz cuvettes and solid-state spectra were recorded in reflectance mode on powdered samples. X-band EPR spectra of both solids and frozen solutions and were recorded at 77 K (using a liquid nitrogen dewar) with a Bruker EMX 10 EPR spectrometer. Elemental analyses for C, H and N were carried out at the Australian National University Microanalytical Laboratory. Prior to being sent for analysis, samples were dried at 40 °C for 48 h under vacuum (0.2 Torr) over phosphorus pentoxide.

Caution: Although no problems were encountered in the course of this work, perchlorate salts are potentially explosive materials and appropriate precautions should be taken when handling them.

***N*-[6-(4-Hydroxyphenyl)-2-pyridylmethyl]-*N,N',N'*-trimethylethylenediamine (HL¹):** A solution of *N,N,N'*-trimethylethylenediamine (363 mg, 3.55 mmol) in 1,2-dichloroethane (15 cm³) was added to a 1,2-dichloroethane (10 cm³) solution of 6-(2-tetrahydropyranyl-4-

phenoxy)-2-pyridinecarbaldehyde (1.000 g, 3.54 mmol) followed by the addition of solid sodium triacetoxyborohydride (0.902 g, 4.25 mmol). The resulting white suspension was stirred for 12 h under nitrogen to give a yellow suspension, which was washed twice with a saturated NaHCO₃ solution (≈ 10 cm³), dried with magnesium sulfate and the solvent removed under vacuum to give the tetrahydropyranyl (THP)-protected precursor, THP-L¹, as a viscous yellow-brown oil (1.130 g). ¹H NMR (CDCl₃): δ = 7.93 (d, 2 H, Ar), 7.67 (d, 1 H, py), 7.54 (t, 1 H, py), 7.33 (d, 1 H, py), 7.12 (d, 2 H, Ar), 5.49 (m, 1 H, CH₂), 3.92 (m, 2 H, CH₂), 3.77 (s, 2 H, CH₂), 3.62 (m, 2 H, CH₂), 2.60 (m, 2 H, CH₂CH₂), 2.49 (m, 2 H, CH₂CH₂), 2.35 (s, 3 H, CH₃), 2.23 (s, 6 H, 2 CH₃), 2.08 (m, 2 H, CH₂), 1.90 (m, 2 H, CH₂) ppm. ESI-MS: *m/z* (%) = 370 (100) [(THP)-L¹ + H]⁺, 286 (10) [H₂L]⁺. Removal of the THP protecting group was effected by heating pyridinium *p*-toluenesulfonate (75.3 mg, 0.30 mmol) and THP-L¹ (1.105 g, 3.00 mmol) in ethanol (50 cm³) at 60 °C for 6 h. The solvent was removed and the resulting solid purified by column chromatography on silica gel with dichloromethane as the eluent; the main yellow band afforded the product, a clear light golden oil (0.810 g, 95%; > 98% purity by ¹H NMR spectroscopy). ¹H NMR (CDCl₃): δ = 7.90 (d, 2 H, Ar), 7.68 (d, 1 H, py), 7.55 (t, 1 H, py), 7.33 (d, 1 H, py), 7.15 (d, 2 H, Ar), 3.88 (m, 2 H, CH₂), 2.70 (m, 4 H, CH₂CH₂), 2.38 (s, 9 H, CH₃) ppm. ESI-MS: *m/z* (%) = 286 (100) [H₂L]⁺. UV (CH₃CN): λ_{max} (ε/dm³mol^{–1}cm^{–1}) = 263 (12400), 284 nm (13400).

***N*-4-(Hydroxybenzyl)methyl-*N,N',N'*-trimethylethylenediamine (HL²):** The literature method^[9] was adapted as follows. A mixture of *N,N,N'*-trimethylethylenediamine (1.502 g, 14.73 mmol), 4-hydroxybenzaldehyde (1.800 g, 14.73 mmol), and sodium triacetoxyborohydride (3.751 g, 17.70 mmol), in 1,2-dichloroethane (70 cm³) was stirred overnight for 16 h under nitrogen. The solvent was removed to give an orange oil that partially dissolved in acetonitrile (≈ 2 × 20 cm³) leaving an off-white solid that was removed by filtering the solution through a short silica plug. Removal of the solvent in vacuo gave the product as an orange-yellow oil (2.822 g, 92%; ≈ 95% purity by ¹H NMR spectroscopy). ¹H NMR (CDCl₃): δ = 7.10 (d, 2 H, Ar), 6.80 (d, 2 H, Ar), 3.59 (s, 2 H, CH₂), 2.92 (t, 2 H, CH₂CH₂), 2.79 (t, 2 H, CH₂CH₂), 2.52 (s, 6 H, CH₃), 2.32 (s, 3 H, CH₃); δ_C (CDCl₃) 157.9 (Ar), 131.8 (Ar), 126.7 (Ar), 116.3 (Ar), 62.1 (CH₂), 54.7 (CH₂CH₂), 52.0 (CH₂CH₂), 44.3 (CH₃), 41.9 (CH₃) ppm. ESI-MS: *m/z* (%) = 209 (100) [H₂L]⁺. UV (CH₃CN): λ_{max} (ε/dm³mol^{–1}cm^{–1}) = 278 (6200), 283 (5900), 314 nm (2900).

***N*-2-Hydroxybenzylmethyl-*N,N',N'*-trimethylethylenediamine (HL³):**^[10] A mixture of *N,N,N'*-trimethylethylenediamine (1.530 g, 15.00 mmol), 2-hydroxybenzaldehyde (1.832 g, 14.99 mmol), and sodium triacetoxyborohydride (3.820 g, 18.03 mmol), in 1,2-dichloroethane (40 cm³) was stirred for 16 h under nitrogen. Workup as for L¹ afforded HL²; a straw-coloured oil (2.780 g, 89%; > 98% purity by ¹H NMR spectroscopy). ¹H NMR (CDCl₃): δ = 7.16 (t, 1 H, Ar), 7.00 (d, 1 H, Ar), 6.83 (d, 1 H, Ar), 6.77 (t, 1 H, Ar), 3.68 (s, 2 H, CH₂), 2.74 (m, 4 H, CH₂CH₂), 2.42 (s, 6 H, CH₃), 2.32 (s, 3 H, CH₃) ppm. ¹³C NMR (CDCl₃): δ = 158.2 (Ar), 129.7 (Ar), 122.5 (Ar), 119.8 (Ar), 117.0 (Ar), 61.2 (CH₂), 56.1 (CH₂CH₂), 53.3 (CH₂CH₂), 44.7 (CH₃), 42.6 (CH₃) ppm. ESI-MS: *m/z* (%) = 209 (100) [H₂L]⁺. UV (CH₃CN): λ_{max} (ε/dm³mol^{–1}cm^{–1}) = 277 (6400), 330 nm (600).

[Cu(HL¹)Cl₂]₂[CuCl₄]: Methanol solutions, 5 cm³ each, of HL¹ (140 mg, 0.49 mmol) and CuCl₂ (66 mg, 0.49 mmol) were stirred overnight. The resulting dark green solution when placed under diethyl ether produced a green precipitate, which was twice recrystallised, firstly from dichloromethane/acetonitrile (3:1) under diethyl ether and then from methanol/acetonitrile (1:1). This pro-

Table 1. Numerical crystal and refinement data for the X-ray crystal structures.

Compound	[Cu(H ₂ L ¹)Cl ₂] ₂ [CuCl ₄]·CH ₃ CN·2H ₂ O	[Cu(HL ²)Cl ₂]	[Cu ₂ (L ³) ₂ (H ₂ O)(ClO ₄)]ClO ₄ ·H ₂ O
Formula	C ₃₆ H ₅₅ Cl ₈ Cu ₃ N ₇ O ₄	C ₁₂ H ₂₀ Cl ₂ CuN ₂ O	C ₂₄ H ₄₂ Cl ₂ Cu ₂ N ₄ O ₁₂
Formula mass	1124.1	342.8	776.6
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>P2₁/c</i>
<i>a</i> [Å]	24.295(6)	14.287(6)	13.597(5)
<i>b</i> [Å]	12.770(2)	8.150(2)	13.937(2)
<i>c</i> [Å]	15.726(4)	26.416(8)	17.152(6)
<i>α</i> [°]	90	90	90
<i>β</i> [°]	91.73(1)	97.65(2)	100.01(2)
<i>γ</i> [°]	90	90	90
<i>V</i> [Å ³]	4877(2)	3048(2)	3201(2)
<i>Z</i>	4	8	4
<i>μ</i> [mm ^{−1}] (radiation)	5.998 (Cu- <i>K</i> _α)	1.780 (Mo- <i>K</i> _α)	1.562 (Mo- <i>K</i> _α)
<i>ρ</i> [g cm ^{−3}]	1.53	1.49	1.61
<i>F</i> (000)	2300.0	1416.0	1608.0
Observed reflections	2339 [<i>I</i> > 2σ(<i>I</i>)]	1844 [<i>I</i> > 3σ(<i>I</i>)]	3470 [<i>I</i> > 3σ(<i>I</i>)]
No. of parameters	264	163	350
Observed reflections	8.9	11.3	9.9
Goodness-of-fit	1.64	1.28	1.54
<i>R</i> ₁ , <i>wR</i> ₂	0.054, 0.073	0.030, 0.039	0.041, 0.051
Max., min. peaks in final difference map [e·Å ^{−3}]	0.61, −0.93	0.52, −0.60	1.07, −1.12

duced X-ray quality, brown, plate-like crystals of [Cu(HL¹)Cl₂]₂·[CuCl₄] (82 mg, 16%). C₃₄H₄₈Cl₈Cu₃N₆O₂·CH₃CN·2H₂O: calcd. C 38.46, H 4.93, N 8.72; found C 38.16, H 4.75, N 8.82. ESI-MS (MeCN): *m/z* (%) = 384 (100) [Cu(HL¹)Cl]⁺, 286 (30) [H₂L¹]⁺. UV (CH₃CN): λ_{max} (ε/dm³mol^{−1} cm^{−1}) = 268 (12400), 288 (13400), 460 (1100), 677 (275), 775 sh (240) nm. UV (solid): λ_{max} (ε/dm³mol^{−1} cm^{−1}) = 690 nm. EPR (CH₃CN glass, 77 K): *g*_{||} = 2.29, *g*_⊥ = 2.09, *A*_{||} = 156 G, *g*_{||} = 2.26, *g*_⊥ = 2.08, *A*_{||} = 120 G; EPR (powder, 77 K) *g*_{iso} = 2.10.

[Cu(HL²)Cl₂]: To HL² (100 mg, 0.48 mmol) in methanol (10 cm³) was added CuCl₂ (65 mg, 0.48 mmol) to give a dark blue solution that was stirred for 2 h. The solution was then reduced to half volume and placed under diethyl ether. After two days standing a green precipitate formed which was collected by filtration and dried under vacuum to give [Cu(HL²)Cl₂] (128 mg, 78%); a portion of this solid was recrystallised from methanol under diethyl ether to give green crystals of sufficient quality for X-ray crystallographic analysis. All data obtained from the powder and crystals were identical. C₁₂H₂₀Cl₂CuN₂O: calcd. C 42.05, H 5.88, N 8.17; found C 41.76, H 5.78, N 8.20. ESI-MS (1% HOAc in CH₃CN): *m/z* (%) = 674 (10) [Cu₂(HL²)₂Cl₂(OAc)]⁺, 331 (40) [Cu(HL²)(OAc)]⁺, 306 (10) [Cu(HL²)Cl]⁺, 209 (100) [H₂L²]⁺. UV (CH₃CN): λ_{max} (ε/dm³mol^{−1} cm^{−1}) = 282 (6200), 379 (1000), 678 (205), 770 sh (190) nm. UV (powder): λ_{max} = 685. EPR (CH₃CN glass, 77 K): *g*_{||} = 2.25, *g*_⊥ = 2.09, *A*_{||} = 153 G; EPR (powder) *g*_{iso} = 2.12.

[Cu₂(L³)₂(H₂O)](ClO₄)₂: Aqueous solutions of L³ (135 mg, 0.65 mmol, in 5 mL) and Cu(ClO₄)₂·6H₂O (240 mg, 0.65 mmol, in 5 mL) were combined to give a black green solution (pH = 5). NaOH (ca. 0.6 mL, 5 M) was added dropwise until a precipitate began to form (pH = 9). The mixture was stirred for 20 h, and then the solid collected by filtration and washed with ethanol, then diethyl ether and dried under vacuum to give the product as a dark green powder (124 mg, 26%). Further product was obtained from the filtrate, which was reduced to half volume then left to slowly evaporate in air. Black, block-shaped crystals (26 mg, 5%) of X-ray analysis quality were obtained. The crystals and the powder exhibited identical spectroscopic data. C₂₄H₃₈Cl₂Cu₂N₄O₁₀·2H₂O: calcd. C 37.12, H 5.45, N 7.21; found C 37.18, H 5.31, N 7.47. ESI-MS (MeCN): *m/z* (%) = 560 (15) [Cu₂(L³)₂(H₂O)]²⁺, 271 (100)

[Cu(L³)]⁺, 209 (30) [H₂L³]⁺. UV (CH₃CN): λ_{max} (ε/dm³mol^{−1} cm^{−1}) = 233 (6800), 278 (6300), 428 (2000), 639 (315). UV (water/ethanol, 1:1, pH = 7): λ_{max} (ε/dm³mol^{−1} cm^{−1}) = 418 (1900), 673 (430) nm. UV (water/ethanol, 1:1, pH = 10): λ_{max} (ε/dm³mol^{−1} cm^{−1}) = 389 (1800), 588 (532) nm; λ_{max} (powder) = 627 nm. EPR (CH₃CN glass, 77 K): *g*_{||} = 2.25, *g*_⊥ = 2.06, *A*_{||} = 165 G; EPR (powder, 77 K): silent.

X-ray Crystallography: Relevant crystal, data collection and refinement data for the X-ray crystal structures of [Cu(H₂L¹)Cl₂]₂·[CuCl₄]·CH₃CN·2H₂O, [Cu(HL²)Cl₂] and [Cu₂(μ-L³)₂(H₂O)(ClO₄)]ClO₄·H₂O are summarised in Table 1.

CCDC-290947–290949 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article). Plots of EPR (at 77 K) and UV/Vis-NIR spectra for all complexes in the solid state and in acetonitrile solution; a figure of a [Cu₂(L³)₂(H₂O)(ClO₄)](ClO₄)·(H₂O)_∞ helix showing hydrogen bond lengths.

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