Paper

# The role of acid in the formation of hydrogen-bonded networks featuring 4,4′-dicarboxy-2,2′-bipyridine ($H_2$dcbp): Synthesis, structural and magnetic characterisation of $\{[Cu(H_2dcbp)Cl_2]\cdot H_2O\}_2$ and $[Cu(H_2dcbp)(NO_3)_2(H_2O)]$

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Reported herein are the synthesis, structural and magnetic characterisation of two hydrogen-bonded networks featuring the 4,4′-dicarboxy-2,2′-bipyridine ($H_2$dcbp) ligand: $\{[Cu(H_2dcbp)(Cl)_2]\cdot H_2O\}_2$ **1** and $[Cu(H_2dcbp)(NO_3)_2(H_2O)]$ **2**. Compounds **1** and **2** result from the reaction of $CuCl_2$ and $Cu(NO_3)_2$, respectively, with $H_2$dcbp under hydrothermal conditions in the presence of either HCl or $HNO_3$. The acid ensures that $H_2$dcbp remains protonated and provides the anions required for charge balance irrespective of Cu(II) precursor. Within **1** and **2** the $H_2$dcbp ligand performs a dual role of Cu(II) coordination, *via* the 2,2′-bipyridine moiety, and propagates the formation of chains through hydrogen-bonding involving the peripheral 4,4′-dicarboxylic acid functionalities. Additional hydrogen bonding between the 4,4′-dicarboxylic acid groups, metal bound chloride and nitrate anions, in **1** and **2** respectively, and water molecules generate 3D networks. Variable temperature magnetic susceptibility measurements reveal very weak antiferromagnetic coupling between the Cu(II) centres across the chloride bridges in **1** ($J = -3.02$ cm$^{-1}$).

## Introduction

An important synthetic strategy currently employed in metallo-supramolecular chemistry utilises ligands that can coordinate to a metal ion through a primary coordination site, while at the same time participate in additional bonding interactions at peripheral sites.[1] These supplementary sites may propagate weaker secondary connections *via* hydrogen bonding[2] or may act as exodentate sites allowing further metal ion coordination.[3] An advantage of the approach is that it may combine the flexibility of the weaker interaction with the strength of coordination bonding. The strategy is best exemplified by considering the poly-carboxylate ligands, which have proven to be particularly effective in the formation of both hydrogen bonded networks and coordination polymers.[4] Pyridine carboxylic acids are also especially useful in this regard, the pyridine nitrogen atom bonding to a metal ion, with the carboxylic acid forming either self-complementary hydrogen bonds to neighbouring ligands, or following deprotonation, coordinating directly to adjacent metal ions.[5] The extension of this approach to functionalised poly-pyridines is particularly attractive, as the coordination chemistry of these ligands is especially rich and the physicochemical properties of the compounds is extremely diverse.[6] In this regard we have employed 4,4′-dicarboxy-2,2′-bipyridine ($H_2$dcbp) as a coordinating ligand in the preparation of coordination polymers and porous metal–organic frameworks.[7] In principle, the 2,2′-bipyridine and carboxylate functional groups of $H_2$dcbp may potentially coordinate to each metal within the periodic table, either singly or in unison. We have also shown that $H_2$dcbp may hydrogen bond through either functionality so the preparation of hybrid networks combining the strength of coordination bonding with the flexibility of hydrogen bonding is also feasible.[8]

We further address this latter point in the current study as a part of our consideration of the weaker (supramolecular) interactions found within coordination clusters and polymers.[9] We describe here the synthesis and structural characterisation of two hybrid networks that result from the combination of coordination and hydrogen bonding. We set out in the current study to utilise the $H_2$dcbp ligand in combination with various Cu(II) salts under acidic conditions. We anticipated that deprotonation would be suppressed, which is facile under non-acidic conditions giving neutral M(II) : dcbp species,[7,8] and favour the retention of the carboxylic acid, which would be available for hydrogen bonding. Various Cu(II) salts bearing univalent anions ($Cl^-$, $NO_3^-$, $AcO^-$) were employed in combination with their acids (HCl, $HNO_3$, HOAc) under hydrothermal conditions, to observe what influence these anions would have upon the structures of the resultant complexes in the knowledge that they would be required for charge balance. The hydrothermal synthetic route was used as it is an attractive method for the fabrication of new materials and the isolation of novel products often different to related examples produced through more conventional syntheses.[10] We report here our success with this approach and present the synthesis and structural characterisation of $\{[Cu(H_2dcbp)(Cl)_2]\cdot H_2O\}_2$ **1** and $[Cu(H_2dcbp)(NO_3)_2(H_2O)]$ **2**. Aspects of the intermolecular interactions found in **1** and **2** are discussed, as is the temperature variable magnetic behaviour of **1**.

## Experimental

### Materials and methods

$CuCl_2\cdot 2H_2O$, $CuNO_3\cdot 3H_2O$, $[Cu_2(OAc)_4(H_2O)_2]$, HCl, $HNO_3$ and HOAc were purchased from Aldrich Chemicals and used as received. $H_2$dcbp was prepared as detailed previously.[11]

Solvothermal syntheses were carried out using a Parr Instrument general-purpose digestion bomb employing a Teflon insert with 45 ml capacity. IR spectra were recorded as KBr pellets on a Perkin Elmer Paragon 1000 FT-IR spectrometer in the 4000–600 cm$^{-1}$ region. Elemental analyses were performed at the Micro-analytical laboratories, University College Dublin.

### Synthesis of {[Cu(H$_2$dcbp)Cl$_2$]·H$_2$O}$_2$ (1)

CuCl$_2$·2H$_2$O (68 mg, 0.4 mmol) and H$_2$dcbp (97 mg, 0.4 mmol) were placed in a 45 ml Teflon-lined digestion bomb with 4 ml water and 2 ml concentrated HCl. The bomb was sealed and placed in the oven where it was heated to 200 °C for 5 hours before slowly cooling to room temperature (3 °C h$^{-1}$). Blue/green crystals were obtained directly in 87% yield. Found: C, 36.07; H, 2.43; N, 6.86; Cl, 17.59%. CuC$_{12}$H$_{10}$N$_2$O$_5$Cl$_2$ requires: C, 36.34; H, 2.54; N, 7.06; Cl, 17.88%. $\nu_{max}$/cm$^{-1}$ (KBr): 3619 w/br, 3428 w/br, 3183 m, 3085 m, 3068 m, 2518 w/br, 1729 vs, 1700 s/sh, 1618 w, 1591 w, 1560 m, 1403 vs, 1376 m, 1290 s, 1238 m, 1211 vs, 1143 s, 1124 w, 1109 w, 971 w, 931 w, 866 w, 825m, 769 m, 754 w, 713 w, 659 s. $\mu_{eff}$(295 K) = 1.96 $\mu_B$.

### Synthesis of [Cu(H$_2$dcbp)(NO$_3$)$_2$(H$_2$O)] (2)

CuNO$_3$·3H$_2$O (97 mg, 0.4 mmol) and H$_2$dcbp (97 mg, 0.4 mmol) were placed in a 45 ml Teflon-lined digestion bomb with 4 ml H$_2$O and 2 ml concentrated HNO$_3$. After sealing the bomb, it was placed in an oven where it was heated to 200 °C for 5 hours and then slowly cooled to room temperature (3 °C h$^{-1}$). A blue solution was obtained from which blue crystals grew on evaporation over a period of three weeks and were isolated in 53% yield. Found: C, 31.83; H, 2.15; N, 12.20%. CuC$_{12}$H$_{10}$N$_4$O$_{11}$: requires: C, 32.05; H, 2.24; N, 12.46%. $\nu_{max}$/cm$^{-1}$ (KBr): 3627 w, 3471 w, 3196 br, 3079 br, 2644 br, 1732 s, 1594 w, 1560 m, 1391 vs, 1292 m, 1212 s, 1143 m, 1126 w, 1072 w, 1023 w, 931 w, 866 w, 826 m, 769 m, 753 w, 713 w, 659 m. $\mu_{eff}$(295 K) = 1.90 $\mu_B$.

### Solvothermal reaction of H$_2$dcbp, Cu(OAc)$_2$·H$_2$O and HOAc

[Cu$_2$(OAc)$_4$(H$_2$O)$_2$] (0.4 mmol) and H$_2$dcbp (0.4 mmol) were placed in a 45 ml Teflon-lined digestion bomb with 4 ml H$_2$O and 1 ml glacial acetic acid. After sealing the bomb, it was placed in an oven where it was heated to 200 °C for 5 hours and then slowly cooled to room temperature (3 °C h$^{-1}$). Small blue crystals were obtained directly in 47% yield. A single crystal X-ray diffraction experiment returned identical cell parameters to that of {[Cu(dcbp)(H$_2$O)$_2$]·2H$_2$O} as previously reported by us.[8a] Found: C, 37.93; H, 3.43; N, 7.25%. CuC$_{12}$H$_{14}$N$_2$O$_8$ requires C, 38.15; H, 3.74; N, 7.41%. $\nu_{max}$/cm$^{-1}$ (KBr) 3398 br, 3303 s/br, 1615 vs, 1553 s, 1485 w, 1423 m, 1382 vs, 1298 m, 1070 w, 919 w, 883 w, 783 m, 706 s, 628 m cm$^{-1}$.

### Crystallographic measurements on 1 and 2

Crystal data and experimental details are summarised in Table 1. Single crystal analyses were performed at 153 K with a Bruker SMART APEX CCD diffractometer using graphite mono-chromated Mo-Kα radiation ($\lambda$ = 0.71073 Å). A full sphere of data was obtained for each using the omega scan method. Data were collected, processed, and corrected for Lorentz and polarization effects using SMART and SAINT-NT software.[12] Absorption corrections were applied using SADABS.[12] The structures were solved using direct methods and refined with the SHELXTL program package.[12] All non-hydrogen atoms were refined anisotropically. Aromatic hydrogen atoms were assigned to calculated positions with isotropic thermal parameters fixed at 1.2 times that of the attached carbon atom. Carboxylic acid and water hydrogen atoms were located from difference maps and refined subject to O–H distance restraints. Despite the quality of the refinement for **2** ($R1$ = 0.0478), a relatively large residual peak of 3 e Å$^{-3}$ was observed in a chemically implausible position. This is most likely due to a disorder in the crystal where the 3 e Å$^{-3}$ residual denotes the metal atom position of a disordered component at low occupancy. Twinning might be another reason for this anomaly, however there was no evidence of a second lattice in the CCD diffraction images.

**Table 1** Crystallographic data for **1** and **2**

| Compound | **1** | **2** |
|---|---|---|
| Chemical formula | $C_{12}H_{10}N_2O_5CuCl_2$ | $C_{12}H_{10}N_4O_{11}Cu$ |
| $M$ | 396.66 | 449.78 |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| $a$/Å | 7.250(2) | 6.4404(4) |
| $b$/Å | 9.346(2) | 9.7045(6) |
| $c$/Å | 11.785(3) | 13.6309(8) |
| $\alpha$/° | 108.400(3) | 76.339(1) |
| $\beta$/° | 98.483(3) | 84.205(1) |
| $\gamma$/° | 108.720(3) | 78.894(1) |
| $V$/Å$^3$ | 689.6(3) | 810.96(9) |
| $Z$ | 2 | 2 |
| $D_{calc}$/g cm$^{-3}$ | 1.910 | 1.842 |
| $\mu$(Mo-Kα)/mm$^{-1}$ | 1.996 | 1.421 |
| $T$/K | 153(2) | 153(2) |
| $R_{int}$ | 0.0323 | 0.0324 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$]$^a$ | 0.0337, 0.0933 | 0.0478, 0.1221 |
| $R_1$, $wR_2$ (all data) | 0.0363, 0.0947 | 0.0547, 0.1255 |
| Reflections: collected, unique, observed | 7458, 2962, 2725 | 8948, 4456, 3899 |

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

CCDC reference numbers 256268 (**1**) and 256269 (**2**).

See http://www.rsc.org/suppdata/ce/b4/b417520d/ for crystallographic data in CIF or other electronic format.

### Magnetic susceptibility measurements

Variable temperature magnetic susceptibility measurements (300–4.2 K) were performed upon powdered samples of **1** at field strength of 1 T using a Quantum Design M.P.M.S. Squid magnetometer following previously reported procedures.[13] Diamagnetic corrections for ligand susceptibilities were made using Pascal's constants and a value of 60 × 10$^{-6}$ cm$^3$ mol$^{-1}$ was used for the temperature-independent paramagnetism of the Cu(II) ion.[14]

## Results and discussion

### Synthesis

As part of our ongoing studies into the coordination chemistry of H$_2$dcbp, we were interested in the synthesis of metal complexes of it following a procedure previously described by Pakkanen who synthesized [Ru(H$_2$dcbp)$_3$]Cl$_2$.[15] Their interests lay in the photophysical aspects of this compound as Ru(II)–H$_2$dcbp complexes have been employed as dye sensitisers in the development of the Graetzel solar cell.[16] Their synthetic method involved hydrothermal reactions under acidic conditions and returned the above complex with the ligand in its protonated form. Whilst we have reported unsuccessful attempts to retrieve analogous Fe(II) and Co(II) complexes following this method,[8a] reactions using Cu(II) proved successful and prompted the current study.[17]

CuCl$_2$ and H$_2$dcbp were reacted under solvothermal conditions in aqueous hydrochloric acid solution at 200 °C for 5 hours. Blue-green crystals were obtained directly from the mother liquor in approximately 87% yield following slow cooling to room temperature. An infrared spectrum showed the presence of H$_2$dcbp ($\nu$(C=O) 1729 cm$^{-1}$) and water (broad bands above 3100 cm$^{-1}$). Partial micro-analytical data were consistent with a 1 : 1 Cu : $H_2$dcbp stoichiometry which reflected that used in the synthesis. The crystals were suitable for a single crystal X-ray diffraction study and the structure determined to be a chloride-bridged Cu(II) dimer: $\{[Cu(H_2dcbp)(Cl)_2]\cdot H_2O\}_2$ **1**. Numerous reactions were performed employing various Cu(II) salts whilst maintaining the same mineral acid (HCl). In all instances crystalline samples of the chloride-bridged dimer, **1**, were returned and thus, it may be concluded that the acid provides the anion regardless of the metal salt employed. Similarly, changing the Cu(II) : $H_2$dcbp ratio to 1 : 2 or 1 : 3 also returned crystalline samples of **1** as the only identifiable product.

Analogous reactions employing $Cu(NO_3)_2$ and $H_2$dcbp in aqueous $HNO_3$, returned a blue solution from which small blue crystals were isolated upon standing in 53% yield. Again IR and elemental analyses were consistent with a 1 : 1 Cu(II) : $H_2$dcbp composition and this was verified by a single crystal X-ray diffraction study which determined the following formulation, $[Cu(H_2dcbp)(NO_3)_2(H_2O)]$ **2**.

The same reaction was performed using $[Cu_2(OAc)_4(H_2O)_2]$ in aqueous glacial acetic acid in an attempt to prepare a corresponding acetate complex which again yielded a crystalline product. Single crystal X-ray diffraction, IR and microanalytical data identified the product as $\{[Cu(dcbp)(H_2O)_2]\cdot 2H_2O\}$, a 2D coordination polymer which we have previously reported.[8a] Despite the presence of acetic acid, the ligand was deprotonated during the reaction, and is probably a consequence of the acetic acid being a weaker acid than either hydrochloric or nitric acid.

## Crystal structure of 1

The atomic numbering scheme and atom connectivity for **1** are shown in Fig. 1. The structure of **1** was refined in the triclinic $P\bar{1}$ space group and crystallographic details are given in Table 1. The structure of **1** consists of a chloride-bridged Cu(II) dimer, in which the $H_2$dcbp ligand remains protonated. The geometry around the copper atom is square pyramidal with the equatorial positions occupied by the chelating $H_2$dcbp nitrogen atoms, a bridging chloride atom and a monodentate chloride atom, and the apical position occupied by another bridging chloride atom. Equatorial bond lengths come in sets of two, the copper to bipyridyl nitrogen, which average 2.03 Å, and the copper to chloride, which average 2.27 Å. Jahn–Teller distortion is clearly present with the axial bond length (2.6929(8) Å) considerably longer than the equatorial bond lengths. Selected bond lengths and angles are presented in Table 2. Further distortion from ideal square-based pyramidal geometry, arises from the bite angle of the $H_2$dcbp nitrogen atoms (N1–Cu1–N2 79.77(7)°). The copper atom is only slightly shifted from the $N_2Cl_2$ basal plane; being displaced 0.053 Å towards the axially coordinated chloride atom. The two halves of the dimer unit are related by inversion, with the inversion centre being at the midpoint between the two copper atoms. The Cl1 atoms bridge the two halves of the complex in a step-wise fashion; with the bipyridine rings sitting perpendicular to the $Cu_2Cl_2$ bridging plane. The metal-to-metal separation in the dimer unit is 3.4441(8) Å. The copper atoms and the bridging chloride atoms sit in the same plane, with no deviation from planarity, and this results in a chloride–chloride separation of 3.617(3) Å. The pyridine rings of $H_2$dcbp are virtually coplanar with a negligible *ca.* 0.8° torsion angle between them. The carboxylate group about C11 is coplanar with the aromatic ring to which it is attached, whereas the carboxylate group about C12 is twisted by *ca.* 15.0° to its corresponding aromatic ring. In contrast to those complexes that contain the deprotonated $dcbp^{2-}$ ligand,[7a,8a] and as expected for protonated carboxylic acids, there are two sets of C–O bond lengths: the carbon to hydroxyl oxygen single bond, which average 1.32 Å, and the carbon to carbonyl oxygen double bond, which average 1.21 Å.

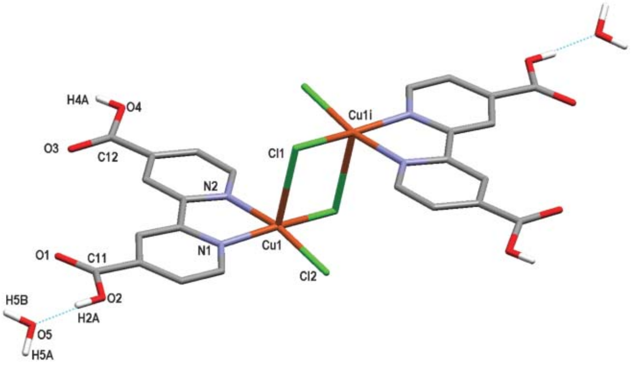

**Fig. 1** Molecular structure and atomic labelling scheme for **1**. The O2–H2A···O5 hydrogen bond is highlighted in blue. Bipyridyl hydrogen atoms omitted for clarity.

**Table 2** Selected bond lengths (Å) and angles (°) for **1** and **2**

| | | | |
|---|---|---|---|
| **1** | | | |
| Cu1–N1 | 2.024(2) | Cu1–Cl1$^i$ | 2.2846(7) |
| Cu1–N2 | 2.035(2) | Cu1–Cl2 | 2.2461(7) |
| Cu1–Cl1 | 2.6929(8) | Cu1···Cu1$^i$ | 3.4441(8) |
| N1–Cu1–N2 | 79.77(7) | N2–Cu1–Cl1 | 94.20(6) |
| N1–Cu1–Cl1 | 95.33(6) | N2–Cu1–Cl2 | 168.98(6) |
| N1–Cu1–Cl1$^i$ | 169.97(6) | Cl1–Cu1–Cl2 | 95.44(3) |
| Cu1–Cl1–Cu1$^i$ | 87.16(2) | Cl1–Cu1–Cl1$^i$ | 92.84(2) |
| **2** | | | |
| Cu1–N1 | 1.985(2) | Cu1–O10 | 1.984(2) |
| Cu1–N2 | 1.986(2) | Cu1–O11 | 1.983(2) |
| Cu1–O7 | 2.231(2) | Cu1···O8 | 2.610(2) |
| N1–Cu1–N2 | 81.78(9) | O7–Cu1–O10 | 78.57(8) |
| N1–Cu1–O7 | 96.46(9) | O7–Cu1–O11 | 89.41(9) |
| N1–Cu1–O10 | 95.94(9) | N2–Cu1–O7 | 112.66(8) |
| N1–Cu1–O11 | 172.21(9) | N2–Cu1–O10 | 168.69(9) |

The dinuclear complexes are linked into a 3D network through hydrogen bond interactions. There are seven unique hydrogen bonds and details of these are gathered together in Table 3. The protonated carboxylic oxygen atom, O4, donates a hydrogen bond to the O1 carboxylic acid oxygen atom of an adjacent complex, while the protonated carboxylic oxygen atom, O2, donates a hydrogen bond to the lattice water molecule, O5. The lattice water molecule, O5, is a hydrogen bond donor to the O3 carboxylic acid oxygen atom on an adjacent complex, and to two chloride atoms on adjacent complexes in a bifurcated manner. The H5B proton sits between a bridging chloride atom, Cl1, and a monodentate chloride atom, Cl2, on that same complex. According to hydrogen-acceptor distances, the former is the major component of the bifurcated hydrogen bond (H5B···Cl1 2.50 Å, H5B···Cl2 2.64 Å). The first three hydrogen bonds can be

**Table 3** Parameters of hydrogen bonding interactions within **1** and **2**

| D–H···A | D–H/Å | *d*(H···A)/Å | *d*(D···A)/Å | <(CH···O)/° |
|---|---|---|---|---|
| **1** | | | | |
| O2–H2A···O5 | 0.83 | 1.69 | 2.525(3) | 174 |
| O4–H4A···O1$^i$ | 0.83 | 1.85 | 2.660(2) | 167 |
| O5–H5A···O3$^{ii}$ | 0.83 | 2.18 | 3.008(3) | 177 |
| O5–H5B···Cl1$^{iii}$ | 0.83 | 2.50 | 3.209(2) | 145 |
| O5–H5B···Cl2$^{iv}$ | 0.83 | 2.64 | 3.300(2) | 137 |
| C4–H4···O3$^i$ | 0.95 | 2.54 | 3.479(3) | 168 |
| C7–H7···O3$^i$ | 0.95 | 2.46 | 3.395(3) | 167 |
| **2** | | | | |
| O2–H2A···O1$^v$ | 0.84 | 1.77 | 2.611(3) | 175 |
| O4–H4A···O7$^{vi}$ | 0.84 | 1.79 | 2.622(3) | 171 |
| O11–H11A···O3$^{vii}$ | 0.84 | 1.87 | 2.687(3) | 163 |
| O11–H11B···O6$^{viii}$ | 0.84 | 2.10 | 2.802(3) | 141 |

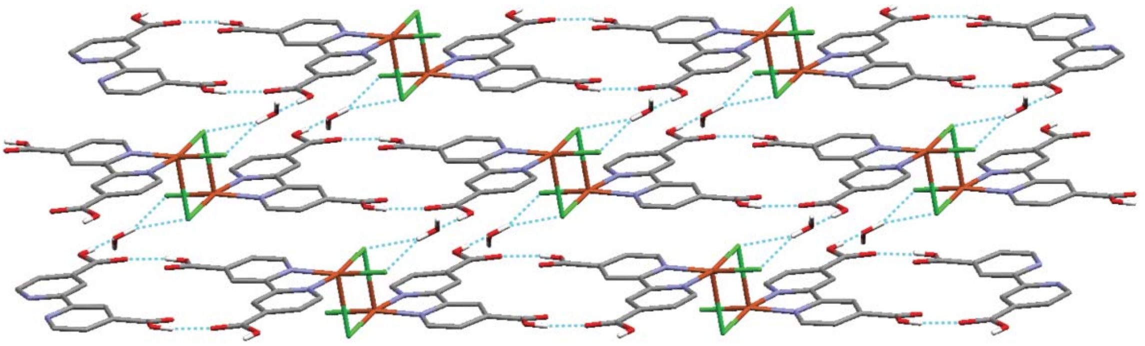

**Fig. 2** The stepped chains in **1** generated through the carboxylic acid interaction (O4–H4A···O1). Hydrogen bonding between chains *via* the water molecule (O2–H2A···O5, O5–H5B···Cl1 and O5–H5B···Cl2) generates a 2D sheet. The second hydrogen atom from the water molecule, H5A, projects above and below the sheet and connects adjacent sheets *via* O5–H5A···O3 to form a 3D hydrogen bonded network. Bipyridyl hydrogen atoms omitted for clarity. Click here to access a 3D image of Fig. 2.

described as being of moderate strength, whereas the latter fall into the weak hydrogen bond category.[18]

The carboxylic acid interaction (O4–H4A···O1) links the complexes into infinite 1D chains as shown in Fig. 2. These ladders are stepped due to the nature of the dinuclear species. Coplanar $H_2$dcbp ligands on adjacent complexes are doubly hydrogen bonded together forming a centrosymmetric $R_2^2(22)$ motif, with the two O3 carboxylic acid oxygen atoms pointing into the middle of the ring.[19] This results in steric repulsion, which forces the carboxylic acid groups to twist with respect to the aromatic ring to which they are attached as noted above. By virtue of its position, O3 acts as a hydrogen bond acceptor from two pyridyl C–H groups (C4–H4···O3 and C7–H7···O3) that further support the $R_2^2(22)$ motif. Fig. 2 shows how the chains are then hydrogen bonded through the lattice water molecule (O2···O5···Cl1/Cl2) to form stepped 2D sheets. Small overlap of the $H_2$dcbp ligands on adjacent ladders gives rise to π–π interactions, with a separation at closest contact of 3.277(3) Å, which reinforces the hydrogen bonded network. The water molecules are aligned within the 2D sheet such that H5A projects either above or below it and forms a hydrogen bond to the carboxylic acid oxygen atom, O3, within adjoining sheets. This interaction connects the sheets into a 3D hydrogen bonded network.

## Crystal structure of 2

The atomic numbering scheme and atom connectivity for **2** are shown in Fig. 3. The structure of **2** was refined in the triclinic $P\bar{1}$ space group and crystallographic details are given in Table 1. The structure of **2** consists of discrete mononuclear $[Cu(H_2dcbp)(NO_3)_2(H_2O)]$ species with square-pyramidal geometry about Cu1. The four basal positions of the pyramid are occupied by the bipyridyl nitrogen atoms, N1 and N2, and two oxygen atoms, one from a coordinated nitrate anion, O10, and the second, O11, from a coordinated water molecule. An oxygen atom, O7, from a second coordinated nitrate anion occupies the apical position of the pyramid. As anticipated by the Jahn–Teller theorem, the axial bond length (Cu1–O7 2.231(2) Å) is longer than the basal bond lengths (average 1.985 Å). The oxygen atom O8 is further distant from Cu1 (Cu1···O8 2.610(2) Å) and projects over the base of the pyramid and is only weakly interacting with Cu1. Selected bond lengths and angles are given in Table 2.

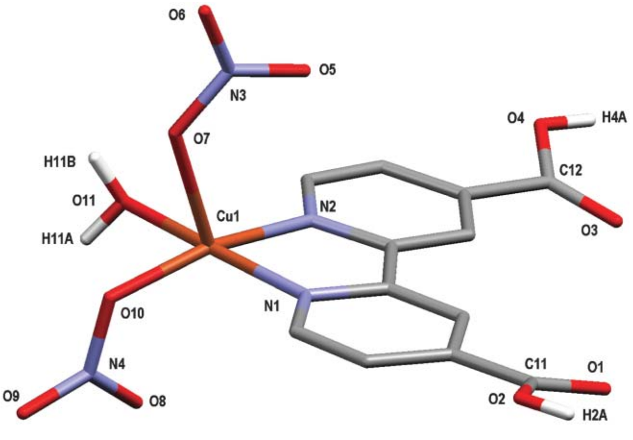

**Fig. 3** Molecular structure and atomic labelling scheme for **2**. Bipyridyl hydrogen atoms omitted for clarity.

The pyridyl rings of the $H_2$dcbp ligand are slightly twisted by *ca.* 2.4° to each other. More pronounced distortion from planarity arises from the twisting of the carboxylate groups with respect to the aromatic rings to which they are attached, with C11 *ca.* 13.2° and C12 *ca.* 15.2° removed from planarity. The carboxylic acid groups remain protonated, as evident from consideration of the C–O bond lengths, with the carbon to hydroxyl oxygen distances (C11–O2 1.284(3) Å, C12–O4 1.314(3) Å) being longer than the carbon to carbonyl oxygen ones (C11–O1 1.247(3) Å, C12–O3 1.213(3) Å). The two coordinated nitrate anions provide the charge balance for the complex. Unlike that found in **1**, where the chloride anions bridge between Cu(II) centres, the nitrate anions in **2** adopt monodentate coordination modes and thus only discrete metal complexes are formed. The N–O bond lengths are longer for the coordinated oxygen atoms (N3–O7 1.287(3) Å, N4–O10 1.293(3) Å) than for the non-coordinated oxygen atoms, which have similar bond lengths to each other due to delocalisation [N3–O5 1.232(3) Å, N3–O6 1.235(5) Å, N4–O9 1.231(3) Å]. The N4–O8 bond length (1.240(3) Å) is also quite short attesting to the weakness of the Cu1···O8 interaction.

There are four unique hydrogen bonds in **2** and details of these are gathered together in Table 3. Each discrete complex interacts with six neighbours through hydrogen bonding. The carboxylic acid centred on C11 participates in a self-complementary hydrogen bond interaction with its neighbour such that the oxygen atom O2 is the hydrogen bond donor to O1 (O2–H2A···O1). The carboxylic acid oxygen atom, O4, is a hydrogen bond donor to the nitrate oxygen atom, O7 (O4–H4A···O7). The coordinated water molecule donates two hydrogen bonds: one to the carboxylic acid oxygen atom, O3 (O11–H11A···O3), and another to the nitrate oxygen atom, O6 (O11–H11B···O6). Two $[Cu(H_2dcbp)(NO_3)_2(H_2O)]$ complexes are connected through the self-complementary carboxylic acid synthon. These extend to form a 1D ladder in combination with the hydrogen bond interaction between the other carboxylic acid and the nitrate anion of an adjacent complex, as shown in Fig. 4a. Further hydrogen bonding between the coordinated water molecule and a carboxylic acid group (O11–H11A···O3) of the ladder above, and between that water and the nitrate anion (O11–H11B···O6) of an adjacent ladder, links them into a 3D network, Fig. 4b. The apparent 'voids' between the steps

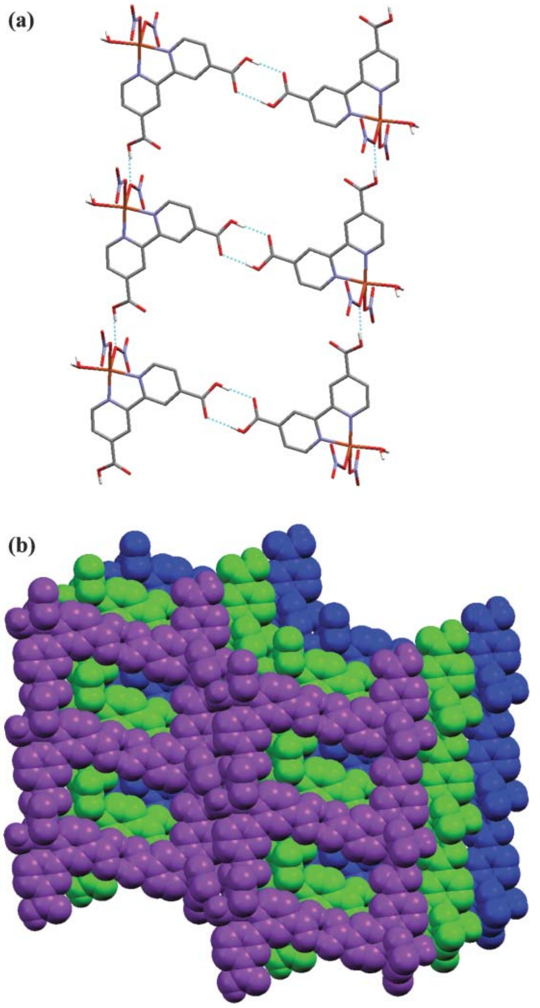

**Fig. 4** **(a)** The ladder in **2** generated through the carboxylic acid hydrogen bond interactions (O2–H2A···O1) and (O4–H4A···O7). Bipyridyl hydrogen atoms omitted for clarity. Click here to access a 3D image of Fig. 4a. **(b)** Hydrogen bonding between ladders (O11–H11A···O3 and O11–H11B···O6) forms a 3D network. Bipyridyl hydrogen atoms omitted for clarity.

of a ladder are filled by the interdigitation of a nitrate anion (centred on N4) from the ladders above and below. Offset face-to-face π–π interactions also occur between the pyridyl rings (the N1 ring overlays the N2 ring) of adjacent stacked ladders with a separation at closest contact of 3.515(4) Å. There is no residual solvent accessible area within **2** attesting to the efficiency of the packing.

### Magnetic properties of 1

The dimeric nature of **1** prompted us to undertake a variable temperature magnetic susceptibility study over the temperature range 4.2–300 K in order to elucidate the nature of any interaction across the chloride bridges. A plot of $\mu_{eff}$ *vs.* $T$ is shown in Fig. 5. Compound **1** displayed typical Curie behaviour between 290 and 100 K remaining practically invariant with temperature at a value of *ca.* 1.95 $\mu_B$, as would be expected for two magnetically isolated spin doublets. A decrease occurred below these temperatures resulting in a value of 0.80 $\mu_B$ at 4.2 K. This behaviour is typical of a very weak antiferromagnetically coupled system. The data were adequately described through a simple Bleaney–Bowers[20] expression for a Cu(II) dimer, derived through the isotropic Hamiltonian $H = -J\ S_1S_2$ where $J$ is the exchange coupling parameter and $S_1 = S_2 = ½$ (interacting local spins). Least-squares fitting leads to the following parameters: $J = -3.02$ cm$^{-1}$, $g = 2.21$ and $R = 5.1 \times 10^{-6}$ (R is the agreement factor defined as $\Sigma_i[(\chi_m T)_{obs(i)} - (\chi_m T)_{calc(i)}]^2/\Sigma_i[(\chi_m T)_{obs(i)}]^2)$.

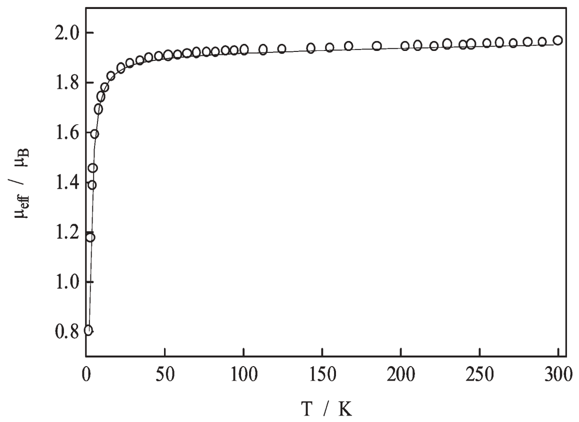

**Fig. 5** The magnetic moment for **1** (per Cu) *vs.* temperature. The solid line is that calculated using the parameters outlined within the text.

The very weak interaction found here is best explained if we consider the magnetic orbital to be of the $d_{x^2-y^2}$ type. The magnitude of the interaction then probably results from the fact that the chloride bridge involves an *axial–equatorial* orthogonal combination, so a ferromagnetic term might be anticipated, and this would offset any antiferromagnetic term and account for its weak nature.[21] The magnitude of the coupling here is in accord with other Cu(II) complexes featuring this bridging disposition.[22] Indeed, Hatfield and Hodgson[22] and more recently Corbella and co-workers[23] have summarized the magnetic data pertaining to di-chloro-bridged Cu(II) dimers of which **1** is a new member. Hatfield has shown that the singlet–triplet gap in such compounds varies regularly with the quantity $\varphi/R$, where $\varphi$ is the Cu–Cl–Cu′ bridging angle and $R$ is the longer Cu–Cl distance. If this quantity lies outside the range 32.6–34.8° Å$^{-1}$ the exchange interaction is anti-ferromagnetic, whereas if it lies within this range it is expected to be ferromagnetic in nature. Several other workers have also verified the validity of the relationship.[24] In the current instance $\varphi/R$ for **1** is 32.36° Å$^{-1}$ and therefore an antiferromagnetic exchange interaction is fully anticipated and indeed is observed.

## Conclusion

We have shown that two polymers $\{[Cu(H_2dcbp)(Cl)_2]\cdot H_2O\}_2$ **1** and $[Cu(H_2dcbp)(NO_3)_2(H_2O)]$ **2**, may be readily synthesised through the hydrothermal reaction, under the relevant acidic conditions, of Cu(II) and $H_2$dcbp. The structures of **1** and **2** have been elucidated and the nature of the intermolecular interactions discussed. Very weak antiferromagnetic coupling was found to be operative within **1** ($J = -3.02$ cm$^{-1}$).

The current study advances our knowledge of the coordinating and hydrogen bonding capabilities of $H_2$dcbp. In our previous investigations we employed neutral or basic conditions, whereas in the present work we deliberately used acidic solutions. It has been previously shown that pH may have an effect on the dimensionality of the resulting structure when employing acidic ligands, with low pH typically leading to low dimensional structures, while higher pH typically leads to higher dimensionality networks.[25] Under the acidic conditions employed here, the $H_2$dcbp ligand remains protonated and therefore cannot coordinate to metal ions through the carboxylic acid groups. Thus, **1** and **2** are low dimensionality coordination complexes. However, as anticipated the $H_2$dcbp ligand does retain the capacity to participate in hydrogen bonding, and thus, the low dimensional complexes are linked into 3D networks through hydrogen bond interactions mediated by the carboxylic acid groups, water molecules and coordinated anions. The isolation of different coordination motifs in **1** and **2** (a dimer *vs.* a discrete complex) is probably a consequence of the dissimilar coordination abilities of the anions, and the nature of the extended networks. We have also shown that it is the acid that provides the anion required for charge balance irrespective of which Cu(II) precursor is present and this most likely stems from the acid (and therefore the anion) being present in large excess. In previous structurally characterised examples incorporating the $H_2$dcbp ligand, the deprotonated ligand provided charge balance and negated the requirement for additional anions. Therefore, an exploration into the various roles anions of dissimilar coordination behaviour may play in the formation of networks incorporating $H_2$dcbp should be very rewarding. We are currently extending our studies to incorporate other transition metal ion and anion/acid combinations. The results from these studies will be reported in due course.

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