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Coordination and hydrogen bonded networks featuring 4,4′-dicarboxy-2,2′-bipyridine (H_2dcbp): structural characterisation of H_2dcbp, [Co(dcbp)$(H_2O)_4$]·$4H_2O$, and {[Cu(dcbp)$(H_2O)_2$]·$2H_2O$}$_n$

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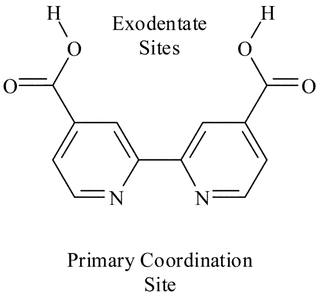
We report herein the single crystal structures of 4,4′-dicarboxy-2,2′-bipyridine, H_2dcbp, and two complexes it forms with Co(II), [Co(dcbp)$(H_2O)_4$]·$4H_2O$, **1**, and Cu(II), {[Cu(dcbp)$(H_2O)_2$]·$2H_2O$}$_n$, **2**. H_2dcbp adopts the *anti* conformation in the solid-state, with a dihedral angle of 148° between each pyridyl ring. Face-to-face $\pi \cdots \pi$ interactions reinforce intermolecular hydrogen bonding (O–H ··· N) involving both carboxylate oxygen and pyridyl nitrogen atoms forming a 2D inter-helical network. Alternate 2D layers are of opposite chirality and are linked into 3D through (C–H ··· O) hydrogen bonds. In both **1** and **2** the ligand is deprotonated giving neutral complexes with 1 : 1 stoichiometry. Although **1** is monomeric, extensive hydrogen bonding between the deprotonated carboxylates, lattice water, and coordinated water molecules results in a 3D network which also contains face-to-face $\pi \cdots \pi$ interactions between adjacent dcbp ligands. Within **2**, pseudo-octahedral coordination about the Cu(II) centre is furnished by bidentate bipyridyl nitrogens, two monodentate carboxylates (from two adjacent dcbp ligands) and two water molecules. Coordination of dcbp in this instance forms a 2D coordination polymer, which is further linked by extensive hydrogen bonding between carboxylates and water molecules, giving a 3D network.

Introduction

It is now seemingly possible within the field of supra-molecular chemistry to select molecular building blocks that will assemble into structures with specific network topologies, so that the rational design of molecular solids with potentially interesting properties is feasible.[1] An important synthetic strategy employed in metallo-supramolecular chemistry utilises ligands that can coordinate to a metal ion through a primary coordination site, while at the same time participating in additional bonding interactions through peripheral sites. These supplementary sites may propagate secondary connections *via* hydrogen bonding[2] or may act as exodentate sites allowing further metal ion coordination, acting as secondary building units (SBU).[3] This approach is best exemplified by considering poly-carboxylate ligands, which have proven to be particularly effective in the formation of both extended hydrogen bonded networks and coordination polymers, some featuring porosity and interesting sorption and host–guest chemistry.[4] Pyridine carboxylic acids have also proven 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 neighbouring metal ions.[5] The extension of this approach to incorporate functionalised polypyridines is particularly attractive, as the coordination chemistry of these ligands is especially rich and the physicochemical properties of the compounds extremely diverse.[6] The periphery of the ligands is also amenable to facile functionalisation. To this end, recent studies by Zubieta and co-workers have included the bipyridine ligand: 5,5′-dicarboxy-2,2′-bipyridine. Hydrothermal syntheses lead to the formation of 2D coordination networks featuring N_2-2,2′-bipyridine bonding about a metal centre and linking through peripheral dicarboxylic acids.[7] This ligand was also usefully employed in the synthesis of organic/inorganic hybrid materials.



In an effort to extend this approach further, we have turned to 4,4′-dicarboxy-2,2′-bipyridine (H_2dcbp), as it potentially has a rich coordination chemistry, with dual chelating capacity through a primary bipyridyl coordination site and exodentate carboxylate sites. The H_2dcbp ligand possesses both chelating and hydrogen bonding capacity at either site. Whilst H_2dcbp has been extensively employed along with Ru(II) as a dye sensitiser in the development of the Graetzel cell,[8] it has been relatively neglected as a ligand incorporating first row transition metals or in the creation of coordination polymers. We are aware of only three recent reports in which H_2dcbp has been employed specifically for this purpose.[9] We have therefore commenced a systematic study of the coordination chemistry of this ligand with a range of transition metals to test its suitability in the formation of extended networks utilising covalent and non-covalent interactions. To this end, we report here the single crystal structure of H_2dcbp, which forms a 2D inter-helical network, and those of [Co(dcbp)$(H_2O)_4$]·$4H_2O$, **1**, and {[Cu(dcbp)$(H_2O)_2$]·$2H_2O$}$_n$, **2**, which each form elaborate 2D/3D networks.

Experimental

$Cu(NO_3)_2.3H_2O$ and $CoSO_4.6H_2O$ were purchased from Aldrich, and used as received. 4,4′-dicarboxy-2,2′-bipyridine was prepared as detailed previously.[10] Na_2dcbp was obtained by adding two equivalents of NaOH to an aqueous suspension of H_2dcbp and evaporating it to dryness. Triply distilled deionised water was employed throughout. IR spectra were recorded as KBr pellets on a Perkin Elmer Paragon 1000 FT-IR

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Table 1 Crystal data for H_2dcbp, **1** and **2**

	H_2dcbp	**1**	**2**
Chemical formula	$C_{12}H_8N_2O_4$	$C_{12}H_{22}CoN_2O_{12}$	$C_{12}H_{14}CuN_2O_8$
Formula weight	244.20	445.25	377.79
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	*Cc*	*Pccn*	*Pnna*
μ(Mo-Kα)/mm^{-1}	0.126	1.032	1.560
a/Å	3.625(1)	6.378(1)	14.7685(9)
b/Å	14.644(5)	12.938(2)	10.8176(7)
c/Å	18.649(7)	21.558(3)	9.0272(5)
α/°	90	90	90
β/°	91.199(5)	90	90
γ/°	90	90	90
V/Å^3	989.8(6)	1778.9(5)	1442.2(2)
Z	4	4	4
T/K	173(2)	173(2)	173(2)
$2\theta_{max}$/°	46.6	56.8	50.0
R_{int}	0.0380	0.0655	0.0555
R_1, wR_2 $[I > 2\sigma(I)]^a$	0.0329, 0.0718	0.0413, 0.0973	0.0532, 0.1059
R_1, wR_2 (all data)	0.0370, 0.0745	0.0572, 0.1022	0.0585, 0.1076
Reflections: collected, unique, observed	4020, 1396, 1300	20361, 2151, 1661	10531, 1276, 1158

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

spectrometer in the 4000–400 cm^{-1} region. ^{1}H NMR spectra were recorded on a Bruker Avance DPX 400 FT spectrometer using TMS as an internal standard. Electrospray mass spectra were carried out on a Shimadzu Micro-mass LCT. Elemental analyses were performed at the Microanalytical laboratories, University College Dublin. Hydrothermal synthesis was carried out using a Parr Instrument general-purpose digestion bomb employing a Teflon insert with 45 ml capacity.

Crystallisation of 4,4′-dicarboxy-2,2′-bipyridine (H_2dcbp)

$FeCl_3$ (0.031 g, 0.19 mmol) H_2dcbp (0.14 g, 0.57 mmol) together with 1 ml of HCl and 2 ml of H_2O were placed in the bomb and heated to 200 °C for 3 h, followed by cooling (3 °C h^{-1}) to room temperature. Long colourless needles of H_2dcbp, suitable for a single crystal diffraction study, were returned in approximately 80% yield. Found: C, 58.72; H, 3.64; N, 11.19%. $C_{12}H_8N_2O_4$ requires C, 59.02; H, 3.30; N, 11.47%. ν_{max}/cm^{-1} (KBr) 3109 w, 2435 m/br, 1860 w/br, 1717 s, 1603 w, 1457 m, 1364 s, 1289 vs, 1267 s, 1241 s, 1137 m, 1065 m, 1010 m, 914 w, 864 w, 819 w, 764 s, 679 s; 516 w. δ_H (400MHz; d_6-DMSO): 8.92 (d, 2H, J = 5 Hz, H6), 8.85 (brs, 2H, H3), 7.92 (dd, 2H, J = 5 Hz, J = 1.5 Hz, H5). MS (ESI): m/z 245.2 [MH]$^+$.

Synthesis of $[Co(dcbp)(H_2O)_4]\cdot 4H_2O$ (1)

Triethylamine (0.15 ml) was added to an aqueous suspension of H_2dcbp (0.05 g, 0.2 mmol) and $CoSO_4\cdot 6H_2O$ (0.018 g, 0.066 mmol) and the mixture was heated to reflux until all the solid had dissolved. On slow evaporation of the yellow solution, needle-like, yellow crystals suitable for a diffraction study were formed in approximately 30% yield. The crystals gradually lose solvent on exposure to air. ν_{max}/cm^{-1} (KBr) 3237 vs/br, 1593 s, 1543 vs, 1422 m, 1380 s, 1292 w, 1262 w, 1234 m, 1152 w, 1120 w, 1082 w, 1043w, 1016 w, 922 w, 787 m, 727m, 700 m, 659 w, 624w, 579 w.

Synthesis of $\{[Cu(dcbp)(H_2O)_2]\cdot 2H_2O\}_n$ (2)

Na_2dcbp (0.1 g, 0.4 mmol) was added to an aqueous solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.096 g, 0.4 mmol) producing a blue precipitate. Adjustment of pH to 10 with dilute NaOH yielded a clear blue solution from which small blue crystals, suitable for a single crystal diffraction study, were obtained directly in 50% yield (0.08 g, 0.2 mmol). The crystals were not sensitive to solvent loss. Found: Cu, 16.84; C, 37.99; H, 3.45; N, 7.29%. $CuC_{12}H_{14}N_2O_8$ requires Cu, 16.82; C, 38.15; H, 3.74; N, 7.41%. ν_{max}/cm^{-1} (KBr) 3395 br, 3307 s/br, 1612 vs, 1556 s, 1482 w, 1428 m, 1380 vs, 1295 m, 1244 m, 1070 w, 1031 w, 919 w, 883 w, 786 m, 704 s, 628 m, 539 m, 470 w.

Crystallographic measurements on H_2dcbp, 1 and 2

Crystal data and experimental details are summarised in Table 1. Single crystal analyses were performed at 173 K with a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 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.[11] Absorption corrections were applied using SADABS.[11] The structures were solved using direct methods and refined with the SHELXTL program package.[11] All non-hydrogen atoms were refined anisotropically. Aromatic hydrogen atoms were assigned to calculated positions using a riding model. Carboxylic acid and water hydrogen atoms were located from difference maps and their positions refined with O–H distance restraints (DFIX 0.84 Å) and isotropic thermal parameters fixed at 1.5 times that of the adjoining oxygen atom. Disordered water hydrogen atoms in **2** were refined at half occupancy.

CCDC reference numbers are 199918 (H_2dcbp), 199919 (**1**), and 199920 (**2**).

See http://www.rsc.org/suppdata/dt/b2/b212318e/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis

Following the previously reported synthetic route to $[Ru(H_2dcbp)_3]Cl_2$,[8d] H_2dcbp, $FeCl_3$, and HCl were reacted under hydrothermal conditions in an attempt to produce the Fe(II) analogue. Single crystals of H_2dcbp were, however, returned in high yield with no precipitation of any iron complex.[12] Complex **1** was synthesised by the addition of triethylamine to an aqueous suspension of $CoSO_4$ and H_2dcbp in 1 : 3 molar ratio at reflux, followed by slow evaporation at room temperature. Reaction of $CoCl_2$ with H_2dcbp (1 : 3) in 50 : 50 DMF/water under hydrothermal conditions produced orange needles, directly. Determination of the unit cell, proved these to be the 1 : 1 polymeric complex $[Co(dcbp)(H_2O)_2]_n$ which was reported recently.[9b] Crystalline samples of complex **2** were isolated following slow evaporation of a basic solution containing equimolar Na_2dcbp and $Cu(NO_3)_2$. Variation of reaction conditions, such as metal to ligand stoichiometry, solvent, or pH, yields a variety of other complexes with Co(II), Cu(II) and other transition metals. Details of these will be presented elsewhere.

Crystal structure of 4,4′-dicarboxy-2,2′-bipyridine (H_2dcbp)

The atomic numbering scheme and atom connectivity for H_2dcbp are shown in Fig. 1. The two pyridyl rings within H_2dcbp are twisted with respect to each other at an angle of approximately 30° from the *anti* conformation, which confers a handedness upon the molecule. Additionally, the carboxylic acid group about C11 is essentially coplanar with the aromatic ring to which it is attached (*ca.* 3° torsion angle) whilst the other about C12 forms an angle of approximately 20°. This further distorts the symmetry of the molecule.

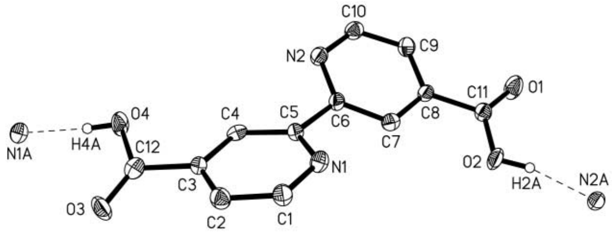

Fig. 1 Molecular structure and atomic numbering scheme in H_2dcbp. Thermal ellipsoids drawn to 50% probability level. Bipyridyl hydrogen atoms omitted. The dotted lines depict the unique hydrogen bonds.

The overall structure of H_2dcbp consists of (4,4) 2D hydrogen bonded sheets as shown in Fig. 2. Each molecule acts as a 4-connector with carboxylate OH groups forming hydrogen bonds to pyridyl nitrogens (O2 ··· N2A = 2.646(3) Å, O4 ··· N1A = 2.669(3) Å). All molecules within a single sheet have the same handedness. Equivalent isonicotinic acid sub-units, *i.e.* crystallographically equivalent halves of the H_2dcbp molecules, reside on the same side of a sheet and hence participate in hydrogen bonding and face-to-face π ··· π interactions (C1 ··· C2* = 3.515(4) Å, N2 ··· C6* = 3.404(4) Å) with like isonicotinic acid sub-units. Hence, each 2D sheet exists as a bilayer containing two sets of parallel hydrogen bonded chains, which are inclined to each other at an angle of 28°. This angle approximately corresponds with the twist in the H_2dcbp molecules from the *anti* conformation.

Each pair of adjacent stacks of the H_2dcbp molecules also form hydrogen bonded helices within each 2D layer that spiral down the crystallographic *a* axis. Since each 2D sheet contains molecules of the same chirality, all helices within a sheet likewise have the same chirality. Alternate layers within the structure contain helices of opposite chirality resulting in an AB type packing of the layers, Fig. 2(b). The structure is nonetheless non-centrosymmetric since layers of alternate chirality are related by glide planes rather than inversion centres. Further intermolecular close contacts are observed between the aromatic protons and carboxylic oxygen atoms both within (H4 ··· O2* = 2.43 Å, H7 ··· O4* = 2.57 Å) and between (H2 ··· O1* = 2.56 Å, H9 ··· O3* = 2.59 Å) the 2D layers, the latter linking the sheets into the third dimension. Full details of all hydrogen bonding interactions are given in Table 2.

It is particularly interesting to compare the solid-state structure of H_2dcbp to those of similar units. Indeed, the 2D helical structure might have been anticipated when consideration is given to the structure of its ‘progenitor’, isonicotinic acid, which consists of head-to-tail hydrogen bonded linear tapes.[13] In this structure however, the adjacent hydrogen bonded chains that participate in π ··· π interactions, are anti-parallel to each other unlike those between the sub-units in the present structure, which are parallel. The head-to-tail arrangement results because the best donor (carboxylic acid) and the best acceptor (pyridine nitrogen atom) form a short intermolecular hydrogen bond. A similar interaction is also found within the solid-state structure of nicotinic acid,[14] although in this instance a zigzag tape results because of the *meta*-substitution (*cf. para*-substitution in isonicotinic acid). This association therefore may be considered predictable, and has been taken advantage of in the crystal engineering of designed solids.[15] In addition to this, the solid-state structures of simple 2,2′-bipyridine and its derivatives are all in the *anti* conformation.[16] Therefore, anticipated structures of H_2dcbp would consist of the 2,2′-bipyridine moiety in an *anti* conformation, accompanied by head-to-tail hydrogen bonding between adjacent carboxylic OH and bipyridyl nitrogen atoms. The formation of simple ‘double’ linear tapes with each half of H_2dcbp running anti-parallel to the other would, however, result in unfavourable steric interactions between aromatic C–H and carboxylic OH groups. The twisting of the two halves of the 2,2′-bipyridine backbone by 30° from the true *anti* conformation avoids this problem while allowing the expected hydrogen bonding and π–π interactions to take place. This arrangement results in helical chains contained within (4,4) 2D hydrogen bonded sheets.

Crystal structure of 1

The atomic numbering scheme and atom connectivity for **1** are shown in Fig. 3. The structure of **1** contains neutral [Co(dcbp)(H_2O)$_4$] units and four lattice water molecules which are linked together through extensive hydrogen bonding into a 3D network. A single complex is shown in Fig. 3 along with the eight crystallographically unique hydrogen bonds. One half of the octahedral Co(II) complex is related to the other by a 2-fold rotation axis which passes through the metal centre and the midpoint of the C1–C1A bond. The bond lengths about Co1

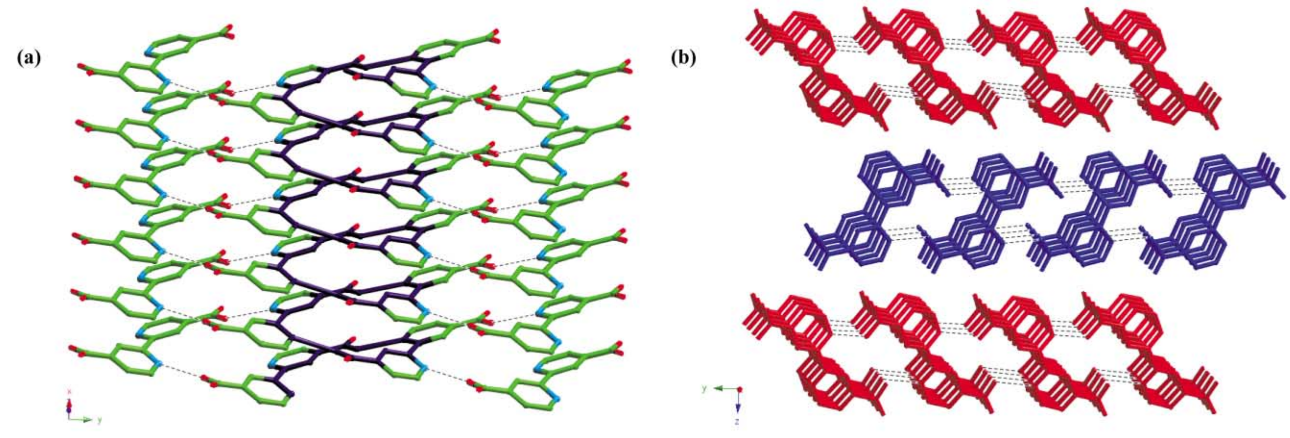

Fig. 2 (a) A single (4,4) 2D hydrogen bonded sheet in H_2dcbp. A single helix is highlighted in purple. Hydrogen bonding within the highlighted helix is represented by solid bonds. (b) The AB packing of the 2D sheets of H_2dcbp. Alternate layers are of opposite chirality (red layers contain right-handed helices).

Table 2 Parameters of hydrogen bonding interactions within H_2dcbp, **1** and **2**

	D–H ··· A	D–H/Å	d(H ··· A)/Å	d(D ··· A)/Å	<(DH ··· A)/°
H_2dcbp	O2–H2A ··· N2^a	0.88	1.79	2.646(3)	166
	O4–H4A ··· N1^b	0.86	1.81	2.669(3)	175
	C2–H2 ··· O1^c	0.95	2.56	3.170(4)	122
	C4–H4 ··· O2^d	0.95	2.43	3.153(3)	133
	C7–H7 ··· O4^e	0.95	2.57	3.106(4)	116
	C9–H9 ··· O3^f	0.95	2.59	3.235(4)	126
1	O1–H1A ··· O4^g	0.81	1.95	2.757(3)	169
	O1–H1B ··· O6	0.81	1.90	2.693(3)	168
	O2–H2A ··· O5^h	0.85	1.87	2.697(3)	166
	O2–H2B ··· O6^i	0.83	1.94	2.732(3)	159
	O5–H5A ··· O3^j	0.84	1.91	2.712(3)	161
	O5–H5B ··· O4^g	0.81	2.01	2.815(3)	173
	O6–H6A ··· O3^k	0.83	1.86	2.690(3)	174
	O6–H6B ··· O5	0.83	2.04	2.817(3)	156
2	O1–H1A ··· O3^l	0.83	2.00	2.790(5)	160
	O1–H1B ··· O1^m	0.84	1.98	2.795(8)	163
	O1–H1C ··· O4^n	0.84	2.00	2.807(6)	164
	O4–H4A ··· O3	0.83	1.98	2.806(5)	178
	O4–H4B ··· O4^o	0.84	2.01	2.839(9)	171
	O4–H4C ··· O1^p	0.83	2.00	2.807(6)	164

Symmetry codes: ^{a} $0.5 + x, y - 0.5, z$. ^{b} $0.5 + x, 0.5 + y, z$. ^{c} $0.5 + x, 0.5 - y, z - 0.5$. ^{d} $x - 0.5, 0.5 + y, z$. ^{e} $x - 0.5, y - 0.5, z$. ^{f} $x - 1, 1 - y, 0.5 + z$. ^{g} $0.5 + x, y - 0.5, 1 - z$. ^{h} $0.5 + x, -y, 0.5 - z$. ^{i} $1 + x, y, z$. ^{j} $x - 0.5, y - 0.5, 1 - z$. ^{k} $x, 0.5 - y, z - 0.5$. ^{l} $0.5 + x, y, 1 - z$. ^{m} $0.5 - x, -y, z$. ^{n} $0.5 - x, -y, 1 + z$. ^{o} $x, -0.5 - y, 0.5 - z$. ^{p} $0.5 - x, -y, z - 1$.

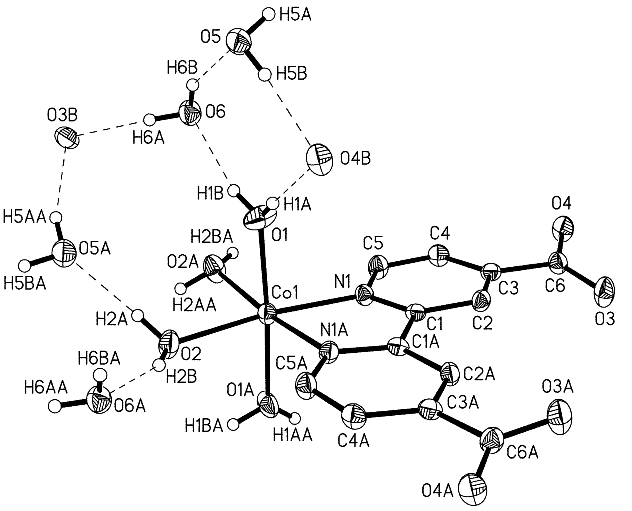

Fig. 3 Molecular structure and atomic numbering scheme in **1**. Thermal ellipsoids drawn to 50% probability level. Bipyridyl hydrogen atoms omitted. The dotted lines depict the eight unique hydrogen bonds.

vary with donor type and position with Co1–O1 2.043(2) Å, Co1–O2 2.096(2) Å and Co1–N1 2.119(2) Å, so distortion from ideal octahedral geometry is evident. More significant distortion from octahedral symmetry is observed in the coordination bond angles, with the chelating dcbp ligand giving a bite angle, N1–Co1–N1A, of 77.7(1)°. The dcbp ligand adopts a near planar conformation with the carboxylate group twisted less than 15° from the plane of the aromatic ring to which it is attached. As expected for a deprotonated carboxylic acid, delocalisation results in identical C–O bond lengths about C6 (C6–O3 1.251(3) Å, C6–O4 1.255(3) Å).

The water hydrogen atoms are ordered throughout the structure as a result of hydrogen bonding. The coordinated water molecule, O1, is a hydrogen bond donor to lattice water, O6, and carboxylate oxygen, O4B, of an adjacent dcbp ligand. The other coordinated water, O2, is also a hydrogen bond donor to lattice water molecules O5A and O6A. The lattice waters themselves exist as hydrogen bonded pairs. Lattice water O5 donates two hydrogen bonds to carboxylate oxygen atoms O4B and O3*, while accepting one hydrogen bond from lattice water O6, and another from a coordinated water, O2*. Lattice water O6 is a hydrogen bond donor to carboxylate oxygen O3B, and acceptor from both coordinated waters, O1 and O2*. Distances and angles for the eight unique hydrogen bonds are listed in Table 2. The overall result of the interactions is a complicated 3D hydrogen bond network, Fig. 4. The [Co(dcbp)(H_2O)$_4$] unit participates in sixteen hydrogen bonds (four coordinated waters and four carboxylate oxygen atoms donate and accept, respectively, two hydrogen bonds each). Double 'bridges' exist between each complex and two other neighbouring complexes accounting for four of the sixteen hydrogen bonds emanating from each complex. The remaining twelve 'bridges' for each complex connect to twelve different lattice water molecules. If a single node represents each pair of lattice water molecules, then the network consists of 14-connecting nodes (complexes) and 6-connecting nodes (pairs of lattice waters) in the ratio 1 : 2. The 14-connecting nodes are joined to two other 14-connectors

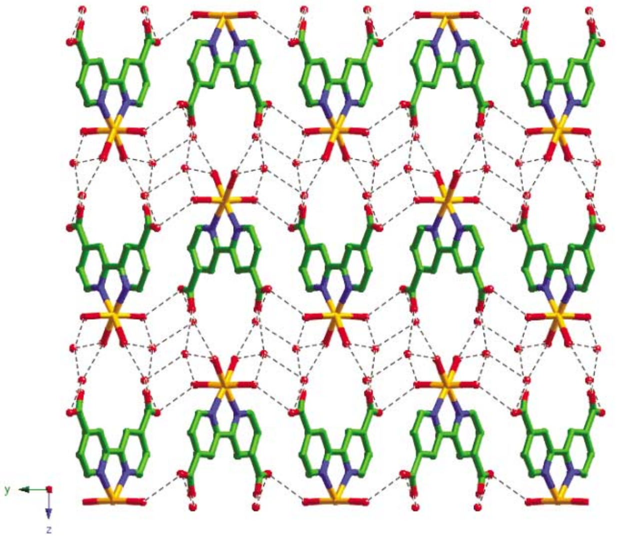

Fig. 4 Packing diagram of **1** as viewed down the crystallographic *a* axis showing the extensive hydrogen bonding.

and twelve 6-connectors while each 6-connector is joined to six different 14-connectors.

The dcbp ligands also participate in π ··· π interactions (C3 ··· C3* = 3.512(5) Å) which form stepped chains propagating in the *a* direction (Fig. 4). Weaker π ··· π interactions (C3 ··· C4* = 3.644(3) Å), with less overlap of the aromatic rings, are observed between adjacent stepped chains giving 2D π-stacked sheets in the *ab* plane (Fig. 4).

Crystal structure of 2

The atomic numbering scheme and atom connectivity for **2** are shown in Fig. 5. The Cu atoms reside on 4*d* Wyckoff positions of the *Pnna* unit cell, hence, like the Co(II) centres of **1**, one half of each Cu(II) environment is related to the other by 2-fold rotation. Three different dcbp ligands occupy the equatorial positions of each Cu(II) atom. Two dcbp ligands coordinate *via* a single carboxylate oxygen (O2) *trans* to the nitrogens of the other chelating dcbp resulting in a neutral 2D coordination polymer of 1 : 1 stoichiometry (Fig. 6). Water molecules (O1) occupy the axial positions on each Cu(II). The pseudo-octahedral centres display typical Jahn–Teller distortion with equatorial bond lengths of 1.960(3) Å (Cu1–O2) and 2.002(4) Å (Cu1–N1) and axial bond lengths of 2.443(5) Å (Cu1–O1). Further distortion from octahedral symmetry can be seen in the *cis* coordination bond angles which range from 80.8(2)° (N1–Cu1–N1A) to 95.0(2)° (N1–Cu1–O1). The dcbp ligands are less planar in comparison to those of **1** with a torsion angle between the aromatic rings of 8°. In contrast to the structures of H_2dcbp and **1**, no π ··· π interactions are observed between the dcbp ligands in the structure of **2**. The carboxylate groups are also twisted at 24° with respect to the aromatic rings. Unlike the carboxylate groups of **1**, which participate only in hydrogen bonding, the C–O bond lengths for **2** differ for the coordinated (C6–O2 = 1.270(6) Å) and uncoordinated (C6–O3 = 1.241(6) Å) oxygens.

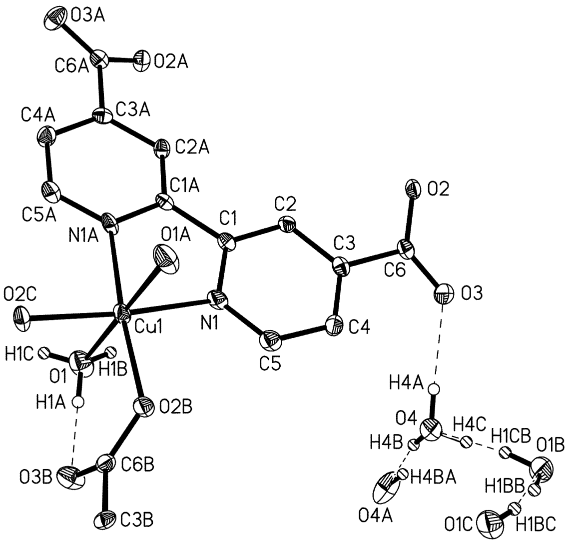

Fig. 5 Atomic numbering scheme in **2**. Thermal ellipsoids drawn to 50% probability level. Bipyridyl hydrogen atoms omitted. The dotted lines depict the unique hydrogen bonds. Shaded hydrogen atoms are at 50% occupancy.

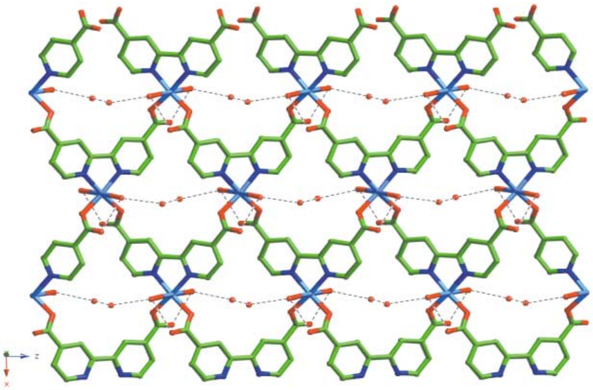

Fig. 6 A single 2D layer in the structure of **2** viewed approximately perpendicular to the sheet. The dotted lines depict the hydrogen bonding within the layer.

The crystal structure contains two unique water molecules, O1 (coordinated) and O4 (lattice). One hydrogen atom position of each is fully occupied and is donated to an uncoordinated carboxylate oxygen. O1 donates H1A to O3B (O1 ··· O3B = 2.790(5) Å) and O4 donates H4A to O3 (O4 ··· O3 = 2.806(5) Å). The remaining hydrogen atom on each water is disordered over two positions (Fig. 5). Full details of hydrogen bonding are given in Table 2. Examination of the hydrogen bond network formed by only the disordered protons reveals 1D infinite helical chains spiralling about two-fold screw axes down the *b* axis. This requires all protons within a single infinite helical hydrogen bonded chain to be ordered since all water molecules must be either donating or accepting protons in the same direction along the chain. Since the structure is centrosymmetric both left and right-handed helical chains are present with those of opposite handedness related by inversion and glide plane symmetry. The positions of the protons in any one helical chain, however, are unable to affect those in adjacent helical chains. Therefore although order of these protons exists in the *b* direction, none exists with respect to the *a* and *c* directions resulting in the overall disordered average for the crystal structure.

The 2D polymer formed by coordination of dcbp to Cu(II) is of (4,4) topology. This assignment considers the metal atoms only as nodes with each node connected to four others through dcbp bridges. It should be noted that if both the metal ion and the dcbp ligand are considered as separate nodes then each would be 3-connecting giving a (6,3) topology for the 2D polymeric sheets in **2**. This node assignment was used in a recent report to describe the topology of the 3D polymer $[Co(dcbp)(H_2O)_2]_n$ as a (12,3) network.[9b] Fig. 6 shows the hydrogen bonding interactions contained within a single 2D layer of **2**. Hydrogen bonding occurs within each Cu(II) coordination sphere between coordinated water and uncoordinated carboxylate oxygen. The lattice waters exist as hydrogen bonded pairs in the 'windows' of the 2D network with one on each side of the mean plane of the sheet, on which all Cu(II) centres reside. These pairs of lattice waters link the Cu(II) centres across the short diagonals of the (4,4) network by hydrogen bonding between coordinated waters on opposite sides of the sheet. Fig. 7 shows the packing of these 2D layers viewed edge on to the sheets and highlights the corrugated nature of the 2D Cu(dcbp) network. There are two types of inter-layer hydrogen bond connections. One is between the coordinated waters on adjacent sheets. The other is between the lattice waters contained within each sheet and the uncoordinated carboxylate oxygen atoms on adjacent sheets.

The overall network resulting from both coordination and hydrogen bonding interactions is represented by the schematic diagram in Fig. 8. The blue nodes represent the Cu atom positions, while the red nodes represent the midpoint of each pair of lattice waters. Hydrogen bonds to coordinated water and carboxylate oxygen atoms are represented by connection to the relevant Cu atom position. The network consists of an equivalent number of 10-connecting and 4-connecting nodes. Each 10-connecting node is linked to six other 10-connectors and four 4-connectors while each 4-connector is linked to four 10-connectors. The six 'shortest circuits'[17] for the 4-connectors all include four nodes. Analysis of the forty-five 'shortest circuits' for the 10-connectors gives thirty-one circuits involving four nodes and fourteen that include six nodes. Therefore the Schläfli notation for the network is $(4^6)(4^{31}.6^{14})$.

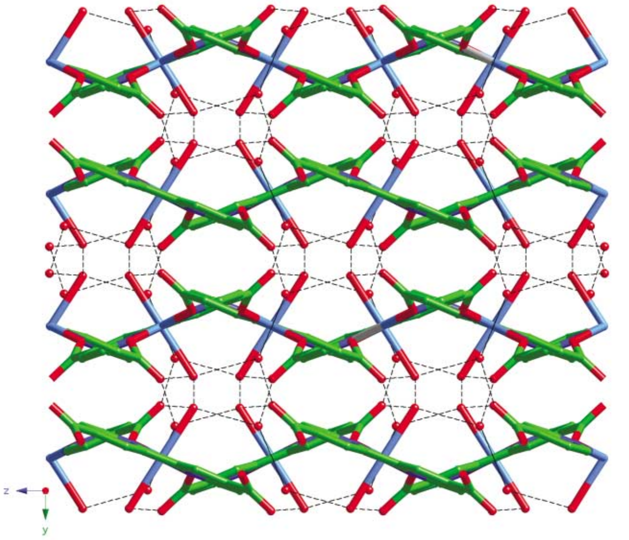

Fig. 7 The packing of the 2D layers of **2** showing both intra- and inter-layer hydrogen bonding connections.

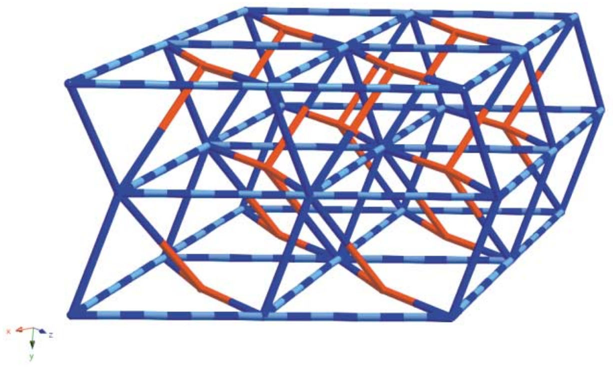

Fig. 8 Schematic diagram for the overall 3D network of **2**. The 10-connecting nodes (blue centres) are the positions of the Cu atoms. The 4-connecting nodes (red centres) represent the midpoint of each pair of lattice water molecules. Blue-banded bonds represent bridging *via* coordinated dcbp (*i.e.* (4,4) sheets). Other bonds represent hydrogen bonding pathways as follows: blue only-between coordinated water, blue/red (in plane of (4,4) sheets)-between coordinated and lattice water, and other blue/red-between lattice water and uncoordinated carboxylate oxygen atoms.

In conclusion, we have successfully demonstrated that H_2dcbp is an extremely versatile ligand not only capable of propagating extended hydrogen bonded and coordination networks, but also combinations of these. As expected, the primary 2,2′-bipyridine and exodentate carboxylate coordination sites are capable of participating fully in hydrogen bond donor/acceptor interactions and coordination to transition metals. Clearly there is great scope with this ligand in the generation of novel coordination and hydrogen bonded networks, which may possess interesting and varied properties. We are currently extending this approach to include other metals of the first and second transition series in addition to those of the lanthanide series and will report upon our recent successes in the near future.

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References

1 (*a*) J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim, 1995; (*b*) *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. Mac Nicol, F. Vögtle and J.-M. Lehn, Pergamon, Oxford, 1996; (*c*) J. W. Steed and J. L. Atwood, *Supramolecular Chemistry: A Concise Introduction*, John Wiley and Sons, 2000; (*d*) G. R. Desiraju, *Nature*, 2001, **412**, 397; (*e*) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546; (*f*) G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray and J. D. Cashion, *Science*, 2002, **298**, 1762; (*g*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1461; (*h*) S. R. Batten, *CrystEngComm*, 2001, **3**, 67.

2 (*a*) C. B. Aakeroy and A. M. Beatty, *Aust. J. Chem.*, 2001, **54**, 409; (*b*) A. M. Beatty, *CrystEngComm*, 2001, **3**, 243; (*c*) A. D. Burrows, C. W. Chan, M. M. Chowdry, J. E. McGrady and D. M. P. Mingos, *Chem. Soc. Rev.*, 1995, 329.

3 (*a*) M. Eddaoudi, D. B. Moler, J. Li, B. L. Chem, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (*b*) B. L. Chem, M. Eddaoudi, S. T. Hyde, M. O'Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021; (*c*) N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe and O. M. Yaghi, *CrystEngComm*, 2002, **4**, 401; (*d*) M. E. Braun, C. D. Steffek, J. Kim, P. G. Rasmussen and O. M. Yaghi, *Chem. Commun.*, 2001, 2532; (*e*) S. A. Bourne, J. J. Lu, A. Mondal, B. Moulton and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2001, **40**, 2111; (*f*) M. Oh, G. B. Carpenter and D. A. Sweigart, *Chem. Commun.*, 2002, 2168; (*g*) S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.

4 (*a*) S. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem., Int. Ed.*, 2000, **39**, 2081; (*b*) H. Li, M. Eddaoudi, M. O'Keefe and O. M. Yaghi, *Nature*, 1999, **402**, 276; (*c*) J. Soo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **402**, 982.

5 (*a*) M. E. Chapman, P. Ayyappan, B. M. Foxman, G. T. Yee and W. B. Lin, *Cryst. Growth Des.*, 2001, **1**, 159; (*b*) C. B. Aakeroy, A. M. Beatty and D. S. Leinen, *Angew. Chem., Int. Ed.*, 1999, **38**, 1815; (*c*) R. Sekiya and S. Nishikiori, *Chem. Commun.*, 2002, 2612; (*d*) C. B. Aakeröy, A. M. Beatty, D. S. Leinen and K. R. Lorimer, *Chem. Commun.*, 2000, 935; (*e*) C. B. Aakeröy, A. M. Beatty and K. R. Lorimer, *J. Chem. Soc., Dalton Trans.*, 2000, 3869.

6 (*a*) C. Kaes, A. Katz and M. W. Hosseini, *Chem. Rev.*, 2000, **100**, 3553; (*b*) M. D. Ward, J. A. McCleverty and J. C. Jeffery, *Coord. Chem. Rev.*, 2001, **222**, 251; (*c*) V. Balzani and A. Juris, *Coord. Chem. Rev.*, 2001, **211**, 97.

7 (*a*) R. C. Finn and J. Zubieta, *Inorg. Chem. Commun*, 2000, **3**, 520; (*b*) R. C. Finn and J. Zubieta, *Solid State Sci.*, 2002, **4**, 83.

8 (*a*) M. Gratzel, *Nature*, 2001, **414**, 338 and references therein; (*b*) A. C. Lees, C. J. Kleverlaan, C. A. Bignozzi and J. G. Vos, *Inorg. Chem.*, 2001, **40**, 5343; (*c*) M. K. Nazeeruddin, S. M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C. H. Fischer and M. Gratzel, *Inorg. Chem.*, 1999, **38**, 6298; (*d*) E. Eskelinen, S. Luukkanen, M. Haukka, M. Ahlgren and T. A. Pakkanen, *J. Chem. Soc., Dalton Trans.*, 2000, 2745.

9 (*a*) T. Schareina, C. Schick and R. Kempe, *Z. Anorg. Allg. Chem.*, 2001, **627**, 1711; (*b*) T. Schareina, C. Schick, B. F. Abrahams and R. Kempe, *Z. Anorg. Allg. Chem.*, 2001, **627**, 131; (*c*) Y. H. Liu, Y. L. Lu, H. C. Wu, J. C. Wang and K. L Lu, *Inorg. Chem.*, 2002, **41**, 2592.

10 A. R. Oki and R. J. Morgan, *Synth. Commun.*, 1995, **24**, 4093.

11 SMART and SAINT-NT, Programs for Data Collection and Data Reduction, Bruker-AXS, Madison, WI, 1998; G. M. Sheldrick, SHELXTL Version 5.0, A System for Structure Solution and Refinement, Bruker-AXS, Madison, WI, 1998.

12 The fact that no Fe(II)–dcbp species was isolated is not surprising since α-diimine complexes such as [Fe(diethyl-2,2′-bipyridyl-5,5′-dicarboxylate)$_3$]$^{2+}$ or [Fe(phen)$_3$]$^{2+}$ are rapidly decomposed under these conditions. See S. G. Telfer, G. Bernardinelli and A. F. Williams, *Chem. Commun.*, 2001, 1498.

13 F. Takusagawa and A. Shimada, *Acta Crystallogr., Sect. B*, 1976, **32**, 1925.

14 M. P. Gupta and P. Kumar, *Cryst. Struct. Commun.*, 1975, **4**, 365.

15 (*a*) M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120; (*b*) C. B. Aakeroy, A. M. Beatty and B. A. Helfrich, *Angew. Chem., Int. Ed.*, 2001, **40**, 3240.

16 *Cambridge Structural Database, Version 5.23*, April 2002, Cambridge Crystallographic Data Centre, Cambridge, *via* www.cmbi.kun.nl.

17 (*a*) A. F. Wells, *Three Dimensional Nets and Polyhedra*, Wiley-Interscience, New York, 1977; (*b*) A. F. Wells, *Further Studies of Three-dimensional Nets*, American Crystallographic Association Monograph No. 8, Polycrystal Book Service, Pittsburgh, PA, 1979.