Coordination Polymers and Metal–Organic Frameworks Derived from 4,4'-Dicarboxy-2,2'-bipyridine and 4,4',6,6'-Tetracarboxy-2,2'-bipyridine Ligands: A Personal Perspective

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Abstract: Presented herein is a personal overview of some of the contributions we have made over recent years to coordination polymer chemistry employing 2,2'-bipyridine-polycarboxylic acid ligands in conjunction with first row transition, main group or lanthanide metal ions. Primarily the discussion is centred upon the two ligands with which we have enjoyed the most success: 4,4'-dicarboxy-2,2'-bipyridine (4,4'-H_2dcbp) and 4,4',6,6'-tetracarboxy-2,2'-bipyridine (4,4',6,6'-H_4tcbp). Initial discussion is focused upon the synthetic aspects of ligand formation and their structural characterisation and then moves on to the synthesis of metal complexes incorporating these ligands and the coordination polymers they form. Where possible the discussion is presented from a synthetic and structural perspective with highlight given to the pertinent properties of the coordination polymers formed *e.g.* thermal behaviour, magnetic, luminescent or small molecule sorption properties. We end the review with some conclusions and highlight some current work with a view to future research.

Keywords: 2,2'-Bipyridine · Coordination polymer · Ligand synthesis · Metal–organic framework · Sorption properties

1. Introduction

There continues to be significant interest surrounding the synthesis and characterization of coordination polymers because of the potential applications within which they may find use.[1] Porous coordination polymers, or metal–organic frameworks (MOFs), in particular attract much attention due to the presence of nanometre-sized voids that may engender commercial applications upon them such as molecular separations, gas storage or sequestration, catalysis and as the active components in sensors.[2]

The polypyridine family of ligands attracts considerable attention as significant chelating ligands due to their ability to form stable complexes with metal ions from across the periodic table.[3] The continued interest is driven by the many properties possessed by these complexes ranging from photochemical and analytical-based materials, through catalytic and electro-catalytic, to anti-proliferative and biological activity.[4] Indeed, the 2,2'-bipyridine-poly-carboxylate based ligands have been used extensively to anchor metal complexes to surfaces and have found utility in dye-sensitised solar cell applications such as within the Grätzel cell.[5] Moreover, considerable current interest surrounds their use in metallo-supramolecular chemistry incorporating the formation of both discrete species (*e.g.* helicates, catenates, *etc.*)[6] and infinite coordination polymers, with porous analogues of the latter attracting great attention as they may possess potential commercial applications derived from their gas storage and sequestration, catalytic, magnetic, host-guest, or sensor capabilities *etc.*[7]

Our attraction to the polypyridine-poly-carboxylate ligands was driven by the fact that, in principle, each functional group may coordinate to every metal within the periodic table in a variety of ways, either singly or in unison, to generate innumerable complexes. The scope of potential coordinating capability of this family of ligands is best exemplified by appreciating the connectivity of the 4,4',6,6'-tcbp ligand (Fig. 1). Indeed, if we couple this connectivity with the ability of the carboxylate ligand coordinated to either single metal ions or to form multi-metallic cluster species, many of which possess interesting magnetic (*e.g.* single molecule magnets) and catalytic properties, then the realization of coordination complexes with myriad properties should be possible. Simply connecting bipyridine coordinated metal ions together through the peripheral carboxylate groups should give rise to the formation of extended frameworks (Fig. 2). Further, hydrogen bonding between ligands through the carboxylic acid functionality would realise hybrid networks combining the strength of coordination bonding with the flexibility of hydrogen bonding.

Despite these potential outcomes and

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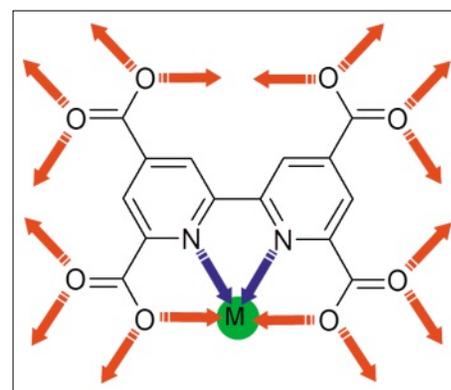
Fig. 1. The structure of 4,4',6,6'-tcbp showing their potential connectivity through carboxylate and 2,2'-bipyridine coordination sites.

the fascinating vista this strategy would provide, there had been only two reports in the literature where the 4,4'-H$_2$dcbp ligand was employed in the deliberate formation of a coordination polymer[8] before our study began although others soon followed,[9] and the 4,4',6,6'-H$_4$tcbp ligand was unknown. With the inspiration to fill this void and to investigate the many properties that such compounds would possess we set about the synthesis of coordination polymers featuring these ligands and provide here an overview of some of our successes in this journey of discovery.

2. A New Synthetic Route to New and Known Polypyridine-poly-carboxylate Ligands

To systematically study the formation and properties of numerous coordination polymers, effective, reliable and, where possible, sustainable synthesis of the poly-pyridine ligands are required. Prior to our modification to the synthesis of carboxylate-containing polypyridine ligands the use of metal-based oxidants, such as K$_2$Cr$_2$O$_7$ and KMnO$_4$, in corrosive media, to generate the carboxylic acid from an appropriate alkyl polypyridines precursor was employed.[10] Whilst this approach has typically wide application, it is encumbered by serious potential health risks and associated waste disposal issues. Indeed, a one gram scale synthesis of 4,4'-H$_2$dcbp involves the slow addition of *ca.* 8.0 g of K$_2$Cr$_2$O$_7$ to 4,4'-dimethyl-2,2'-bipyridine and generates litres of acidic aqueous waste solution for disposal after work-up. We therefore developed a simple method employing dilute aqueous nitric acid solutions (4%) following a solvothermal protocol using a Teflon-lined digestion bomb to give crystalline products in a single step in better yields than those achieved through traditional methods.[11] Simple product recovery through filtration yields a recyclable filtrate (Scheme 1).

This method is superior to traditional metal-based oxidation routes from an environmental point-of-view, as it does not require any subsequent work-up which negates hazardous waste disposal issues, and also allows access to novel molecules that are inaccessible *via* these routes. It is applicable across symmetrical and unsym-

metrical substituted alkyl-polypyridine molecules including bi-, ter- and quater-pyridine examples. Indeed, when using more forcing conditions oxidation may be accompanied by decarboxylation. For example, oxidation of 4,4',6,6'-tetramethyl-2,2'-bipyridine in 2:1 H$_2$O/HNO$_3$ solution at 160 °C is accompanied by regioselective mono-decarboxylation at the 6'-carboxylic acid position to yield crystalline 4,4',6-tricarboxy-2,2'-bipyridinium nitrate hydrate in *ca.* 50% yield (see section 4.1).[12] This method is, therefore, a viable route to the synthesis of this unsymmetrical product, which would be difficult to obtain through more conventional synthetic means.

Fig. 2. The structures of metal complexes of 4,4'-dcbp and 4,4',6,6'-tcbp showing their potential connectivity through carboxylate coordination sites to form extended coordination frameworks.
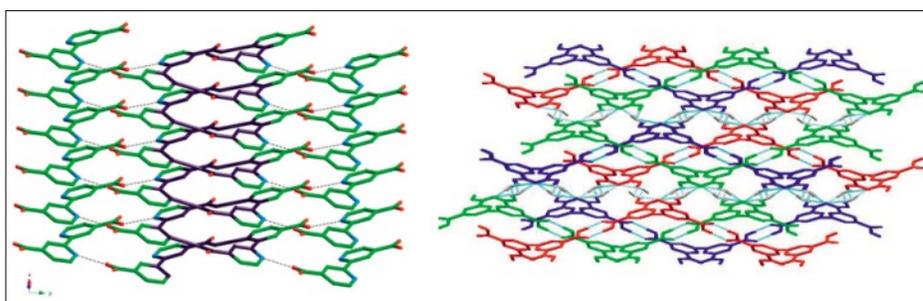
Fig. 3. A single (4,4) 2D hydrogen-bonded sheet in 4,4'-H$_2$dcbp with a single helix highlighted in purple (left) and the 3-fold 2D→2D parallel interpenetrated hydrogen-bonded networks of 4,4',6,6'-H$_4$tcbp (right). The networks are shown in blue, red and green. Adapted from refs. [13] and [14]. Reproduced by permission of the Royal Society of Chemistry.

2.1 *Structural Characterisation of 4,4'-H$_2$dcbp and 4,4',6,6'-H$_4$tcbp Ligands*

When working with poly-carboxy-polypyridine molecules it is immediately apparent that they have extremely limited solubility in common laboratory solvents, so much so that prior to our work the solid-state structures of both 4,4'-H$_2$dcbp and 4,4',6,6'-H$_4$tcbp were unknown. This insolubility then places some restriction upon the synthetic methods used in the formation of coordination complexes and polymers, as it does upon the recrystallisation of the ligands. We set about to ascertain their solid-state structures through single X-ray diffraction and found that solvothermal recrystallisation was effective *i.e.* simply heating either 4,4'-H$_2$dcbp or 4,4',6,6'-H$_4$tcbp in water at 150 °C in a sealed Teflon-lined digestion bomb in the presence of a drop of nitric acid yielded single crystals following slow cooling (Fig. 3).[13,14]

The structure of 4,4'-H$_2$dcbp consists of two-dimensional (2D) hydrogen-bonded
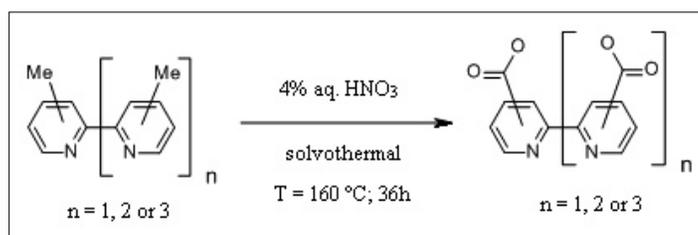
Scheme 1. Polypyridine substrates used to generate the corresponding polypyridine-polycarboxylic acids *via* aqueous nitric acid oxidation under solvothermal conditions.

sheets of (4,4) topology.[13] Each molecule acts as a four-connector with carboxylic acid groups forming hydrogen bonds to pyridyl nitrogen atoms. Equivalent isonicotinic acid sub-units, *i.e.* crystallographically equivalent halves of the 4,4'-H$_2$dcbp molecules, reside on the same side of a sheet and participate in hydrogen bonding and face-to-face π···π interactions 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 4,4'-H$_2$dcbp molecules from the *anti* conformation.

4,4',6,6'-H$_4$tcbp crystallises as a dihydrate and its overall structure consists of hydrogen-bonded chains linked *via* an R$^2_2$(8) dimer motif involving the 4- and 4'-carboxylic acid groups.[14] Hydrogen bonding involving the 6- and 6'-carboxylic acid groups and water molecules link these chains to one another through an R$^4_4$(12) motif to form a wavelike 2D hydrogen-bonded grid. The 'aperture' within the 2D grid is of sufficient size to allow additional 2D grids to pass through it to yield layers of 3-fold 2D → 2D parallel interpenetrating networks. The interwoven networks are then further cross-linked into a single, overall three-dimensional (3D) network *via* further, longer interactions between the water molecules and carboxylic acid groups. It is clear that the extensive hydrogen bonding and π-π interactions within both 4,4'-H$_2$dcbp and 4,4',6,6'-H$_4$tcbp give rise to their lower solubility.

3. Coordination Polymers of 4,4'-H$_2$dcbp and Transition Metal Ions

When an aqueous solution of Cu(NO$_3$)$_2$ was allowed to react with the sodium salt of 4,4'-dcbp in a 1:1 molar ratio, and the pH of the solution brought to ~10 by addition of dilute NaOH, small, blue crystals grew on evaporation which were structurally determined to be {[Cu(4,4'-dcbp)(H$_2$O)$_2$]·2H$_2$O}, a 2D coordination polymer (Fig. 4).[13] The 2D polymer formed by coordination of 4,4'-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 4,4'-dcbp bridges. Heating the crystals led to loss of crystallinity and of coordinated and lattice water molecules by 82 °C, with decomposition setting in at *ca.* 310 °C. A variable temperature magnetic susceptibility study revealed very weak antiferromagnetic coupling between Cu(II) centres ($J = -0.29(1)$ cm^{-1}) consistent with the long distance between Cu(II) centres across the ligand within a 2D sheet, and through co-
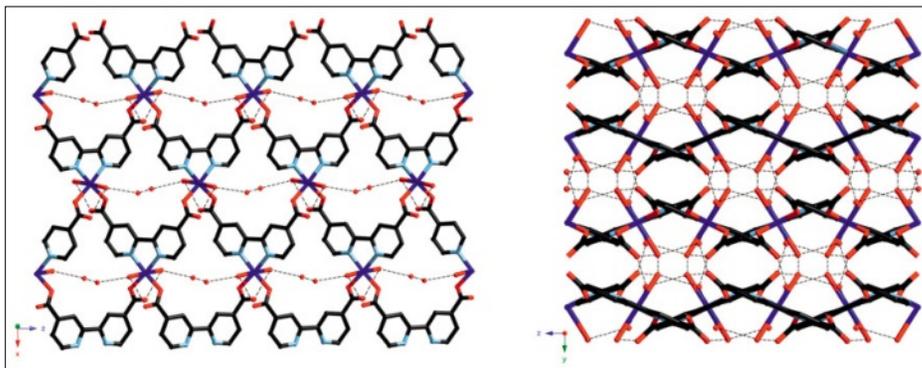
Fig. 4. A single 2D layer in the structure of {[Cu(4,4'-dcbp)(H$_2$O)$_2$]·2H$_2$O} viewed approximately perpendicular to the sheet (left) and the packing of the 2D layers showing both intra- and interlayer hydrogen bonding connections (right). The dotted lines depict the hydrogen bonding.
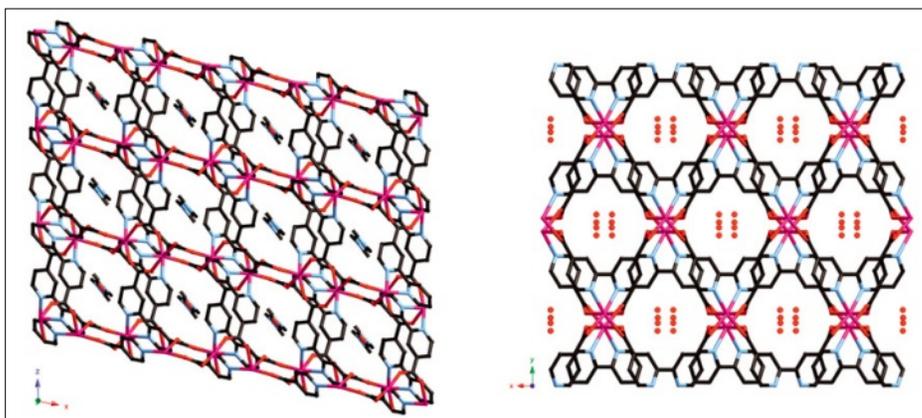
Fig. 5. The structures of {[Mn(dcbp)]·½DMF} showing the channels occupied by disordered DMF molecules (left) and {[Mn(dcbp)]·2H$_2$O} showing disordered water molecules in the channels.

ordinated water molecules between the sheets.

Using standard bench-top synthetic methods consistently yielded either discrete or lower dimensionality polymeric species so we then turned to solvothermal synthesis. Solvothermal synthesis has become a standard method for the preparation of coordination polymers as it provides access to high liquid temperatures, due to the autogenous pressure produced within the sealed reaction vessel, which helps to promote self-assembly processes.[15] Indeed, it also helps to circumvent the solubility issues encountered when using bench-top methods. Adopting a solvothermal protocol we first investigated the synthesis of 4,4'-H$_2$dcbp complexes of Mn(II), Co(II), and Ni(II) employing either neat or mixed water, dimethylformamide (DMF) or diethylformamide (DEF) solvent regimes and structurally identified: {[Mn(4,4'-dcbp)]·½DMF}, {[Mn(4,4'-dcbp)]·½DEF}, {[Mn(4,4'-dcbp)]·2H$_2$O}, α-[Co(4,4'-dcbp)(H$_2$O)$_2$], β-[Co(4,4'-dcbp)(H$_2$O)$_2$] and [Ni(4,4'-dcbp)(H$_2$O)$_2$] species.[16,17] In each complex the ligand is doubly deprotonated giving neutral species with 1:1 stoichiometry that form three-dimensional (3D) coordination polymers. The identity of the polymer formed by Mn(II) and 4,4'-H$_2$dcbp depends upon

the predominant solvent employed in the synthesis and yields robust network isomers: {[Mn(4,4'-dcbp)]·½DMF}, {[Mn(4,4'-dcbp)]·½DEF}, and {[Mn(4,4'-dcbp)]·2H$_2$O}. The frameworks formed when using DMF and DEF complexes are iso-structural to each other but different to that isolated when using water (Fig. 5).

The carboxylate groups in {[Mn(4,4'-dcbp)]·½DMF} join adjacent Mn centres to produce *bis*-carboxylato bridged chains that further cross-link through 4,4'-dcbp to generate the 3D network. The network has channels along *a*, *b*, and *c* axes that constitute 23.3% of the crystal volume and contain large voids at their points of intersection, which are occupied by disordered DMF guests. TGA of {[Mn(4,4'-dcbp)]·½DMF} showed that it is exceptionally robust and stable to guest loss up to 410 °C, after which decomposition begins. Guest loss normally precedes host decomposition, however it appears in this instance that DMF is too large to fit through the apertures of the pores and is therefore irreversibly trapped within the host network. As a consequence of the larger steric profile of DEF, small but significant changes are observed within the molecular structure of {[Mn(4,4'-dcbp)]·½DEF} compared to {[Mn(4,4'-dcbp)]·½DMF}, and the crystal cell parameters vary slightly and result in

an overall cell volume increase of 1.3%. The need to accommodate a bigger guest molecule forces the expansion of the channels such that they now constitute 24.4% of the crystal volume and more greatly distorts the 4,4'-dcbp ligand. The Schläfli notation[18] for the networks is: $(4.6^2)(4^2.6)(4^3.6^6.8^6)$, and is arrived at by considering the Mn(II) centres as six-connectors and each 'isonicotinate half' of the 4,4'-dcbp ligand as three-connectors in the ratio 1:2. Although there is only one type of six-connector, topologically there are two types of three-connectors arising from the crystallographic inequivalence of each half of the 4,4'-dcbp ligand. The coordination network of {[Mn(4,4'-dcbp)]·½DEF} is topologically identical to that of {[Mn(4,4'-dcbp)]·½DMF}, since the connectivity is the same.

The resultant magnetic moments per manganese for {[Mn(4,4'-dcbp)]·½DMF} and {[Mn(4,4'-dcbp)]·½DEF} decreases gradually from *ca.* 5.80 μ_B to *ca.* 5.35 μ_B between 300 and 80 K, respectively, and then more rapidly to 1.40 μ_B at 4.2 K. This behaviour is typical for weak antiferromagnetically coupled high spin octahedral Mn(II) centres combined with zero-field splitting at low temperatures. The μ_B values at low temperature remain essentially independent of field indicating no long-range antiferromagnetic order was present.

The coordination sphere about the Mn(II) centre in {[Mn(4,4'-dcbp)]·2H$_2$O} is very similar to those found in the DMF/DEF analogues although their network topologies are completely different. In contrast to the DMF/DEF analogues, all carboxylate chains in {[Mn(4,4'-dcbp)]·2H$_2$O} run parallel to each other. The network is not as heavily perforated with only two directions containing channels of appreciable dimension. The water molecules reside in the channels and hydrogen-bond to each other and to the carboxylate groups. The channels in {[Mn(4,4'-dcbp)]·2H$_2$O} constitute 18.2% of the crystal volume. TGA showed that the water molecules are rather weakly bound and vacate the pores before 65 °C with the network remaining intact up to 410 °C. When a single crystal of {[Mn(4,4'-dcbp)]·2H$_2$O} was heated to 70 °C on the X-ray diffractometer and a new data set collected, the structure of the 'guest-free' host [Mn(4,4'-dcbp)] was revealed and retains its porous nature, which now accounts for 17.0% of the crystal volume. Furthermore, when crystals of [Mn(4,4'-dcbp)] were exposed to humid air on cooling, {[Mn(4,4'-dcbp)]·2H$_2$O} was regenerated showing the reversibility of the desorption–adsorption process.

The different connectivity of the network in {[Mn(4,4'-dcbp)]·2H$_2$O}, compared to that of the DMF/DEF analogues, is highlighted by its $(4^2.6)(4^4.6^2.8^8.10^1)$

Schläfli symbol. Only one descriptor is needed for the three-connected nodes since the two halves of 4,4'-dcbp ligand are related by symmetry. Since, in each of these complexes, each Mn(II) centre connects to five 4,4'-dcbp ligands, and *vice versa*, a five-connected network could be assigned using a similar approach to that which gives a (12,3) topology for [Co(4,4'-dcbp)(H$_2$O)$_2$] and [Ni(4,4'-dcbp)(H$_2$O)$_2$] complexes (see later). If this were the case the Schläfli notation for each {[Mn(4,4'-dcbp)].solv} species would be the same, condensing to $(4^6 6^4)$ since both metal and ligand nodes have the same shortest circuits. This highlights the value of considering each isonicotinate half of the 4,4'-dcbp ligand separately to distinguish between the different topologies of these systems.

The porosity in [Mn(4,4'-dcbp)] and the nature of the channels within it have recently been identified to have potential utility in gas separation. In 2012 a report[19] detailed the results of a computational screen of over 3,400 coordination polymers with experimentally confirmed crystal structures for performance in three binary rare gas separations: Ar/Kr, Kr/Xe, and Xe/Rn by applying Ideal Adsorbed Solution Theory (IAST) and parameterisation using GCMC calculations. For each binary separation, materials were identified with predicted performance that surpasses the current state-of-the-art. A significant number of materials were found to be 'reverse selective' meaning that a smaller gas species is preferably adsorbed over a larger species; the origin of this being attributed to better size matching between the pore and the selected gas. Of the >3,400 polymers screened, {[Mn(4,4'-dcbp)]}, was predicted to be the best and an excellent candidate for further research into its applicability to Kr/Xe separations. The strongest separation predicted was at 0.1 bar with a selectivity of 12,500 at 298 K: when the temperature was decreased to 77 K, the simulation did not record any Xe being adsorbed at all, indicating nearly perfect selectivity. Naturally, experimental

verification of these findings would be a significant step toward the use of these materials in practical applications.

Supramolecular isomerism (polymorphism) is observed in [Co(4,4'-dcbp)(H$_2$O)$_2$] networks, denoted by us as α and β, and arises from the different ligand connectivity around the octahedral Co(II) centres.[17] The two coordinated water molecules in the α-polymorph occupy *cis* positions, which are *trans* to the chelating bipyridine nitrogen atoms, leaving the carboxylate oxygen atoms in axial *trans* positions. In the β-polymorph all like donors occupy *cis* positions. Different modes of carboxylate coordination in the α and β polymorphs give dissimilar network topologies. A rare example of two interpenetrating $6^4 8^2$-b (quartz-like) chiral networks in β-polymorph results from both 4,4'-dcbp carboxylate groups coordinating in a monodentate fashion to adjacent Co(II) centres (Fig. 6), whereas in β-polymorph only one carboxylate group bridges between adjacent Co(II) centres giving rise to a single chiral (10,3)-a net (Fig. 7). [Ni(4,4'-dcbp)(H$_2$O)$_2$] is isomorphous with α-[Co(4,4'-dcbp)(H$_2$O)$_2$] and likewise features two chiral interpenetrating nets of quartz topology.[17] Strikingly for a pair of dimorphs the crystal densities differ by *ca.* 0.3 g cm^{-3} (1.654 *vs.* 1.940 g cm^{-3}, respectively). Representative magnetic susceptibility studies performed upon these complexes reveal very weak antiferromagnetic coupling between the metal centres in each case.

3.1 Coordination Polymers of 4,4'-H$_2$dcbp and Transition Metal Ions: The Role of Acid

In a parallel study we set out to utilise the 4,4'-H$_2$dcbp ligand in combination with various Cu(II) salts under acidic hydrothermal conditions.[20] We anticipated that deprotonation would be suppressed and favour the retention of the carboxylic acid, which would be available for hydrogen bonding. Various Cu(II) salts (Cl$^-$, NO$_3^-$, AcO$^-$, SO$_4^{2-}$) were used in combina-
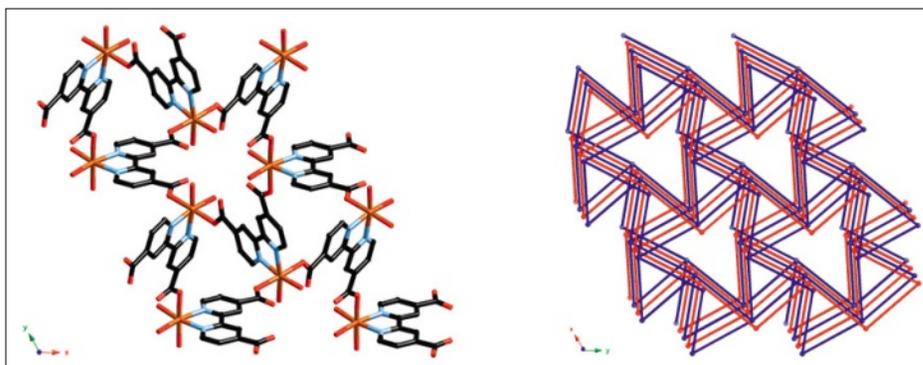
Fig. 6. Packing diagram of α-[Co(4,4'-dcbp)(H$_2$O)$_2$] viewed down the crystallographic *c*-axis (left) and the schematic of the two interpenetrating $6^4 8^2$-b (quartz-like) nets viewed along *c* (right). Adapted from ref. [17]. Reproduced by permission of the Royal Society of Chemistry.
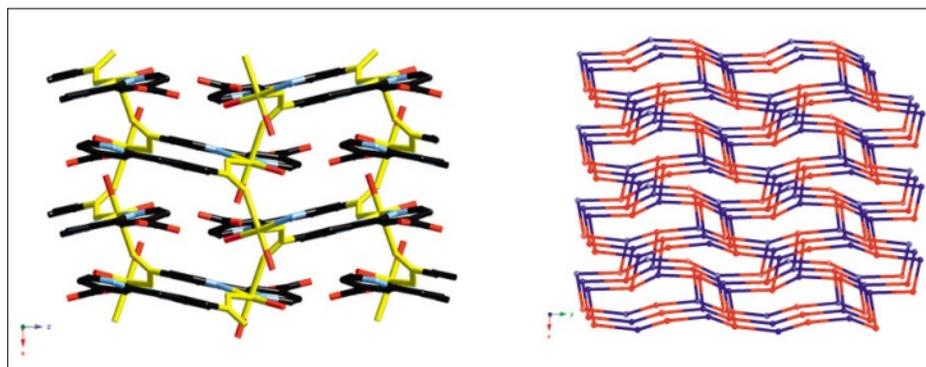
Fig. 7. Packing diagram of β-[Co(4,4'-dcbp)(H$_2$O)$_2$] viewed down (010) showing the carboxylato-cobalt chains spiralling down the *a*-axis high-lighted in yellow (left) and schematic of the (10,3)-a net as viewed *ca.* along *c*. Adapted from ref. [17]. Reproduced by permission of the Royal Society of Chemistry.
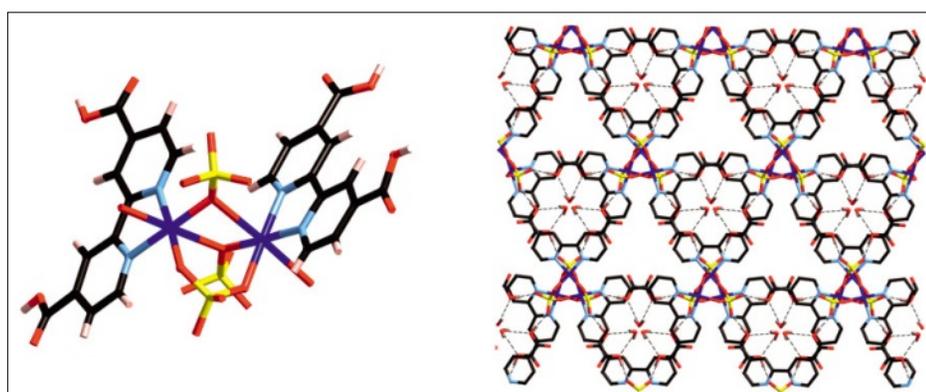
Fig. 8. Detail of a tri-sulfate bridged Cu(II) dimer in {[Cu(4,4'-H$_2$dcbp)(SO$_4$)]·⅓H$_2$O} (left) and the 3D hybrid polymer it forms (right). Hydrogen bonding and π-π interactions between adjacent 1D polymers give rise to channels along the *c* direction. Channels on the 3$_1$ axes are occupied by disordered water molecules, while those on the 3-fold rotation axes are void of solvent.

tion with their acids (HCl, HNO$_3$, HOAc, H$_2$SO$_4$) 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. This approach successfully produced coordination polymers where the 4,4'-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, nitrate or sulfate anions and water molecules generated hybrid 3D networks. The Cu(OAc)$_2$/HOAc combination yielded {[Cu(4,4'-dcbp) (H$_2$O)$_2$]·2H$_2$O} as seen earlier. The most interesting species was {[Cu(4,4'-H$_2$dcbp) (SO$_4$)]·⅓H$_2$O} within which the Cu(II) ion adopts a distorted octahedral geometry, with two of the equatorial positions occupied by the chelating nitrogen atoms of the 4,4'-H$_2$dcbp ligand, and the remaining equatorial and the two axial positions occupied by oxygen atoms of four adjacent sulfate anions (Fig. 8).[21,22]

Each of the coordinated sulfate oxygen

atoms does so in a bidentate fashion, and hence each sulfate anion bridges four copper centres. Bridging of the metal centres by sulfate anions gives rise to a one-dimensional (1D) polymer extending along the crystallographic *c* axis. Adjacent [Cu(4,4'-H$_2$dcbp)(SO$_4$)] units are related by 3$_1$ screw axes, thus forming left-handed helices. All chains within the structure are left-handed and therefore it is chiral (however, the batch of crystals was racemic). The Cu(II) ions are solely bridged by the anions, with 4,4'-H$_2$dcbp merely acting as a terminating ligand. Packing of the 1D polymer gives rise to channels. The protonated oxygen atom of the carboxylic acid group in 4,4'-H$_2$dcbp is a hydrogen-bond donor to the non-coordinating sulfate oxygen atom of an adjacent chain. There are two types of channels in the structure: those that lie on 3-fold axes and those that lie on 3$_1$ screw axes. The channels on the 3-fold axes have dimensions of 4.00 × 5.14 Å, while those on the 3$_1$ axes are slightly smaller with dimensions of 4.24 × 4.47 Å. Together they constitute 8.5% of the total crystal volume. While the former channels are void of solvent, in the latter reside the water molecules. These are disordered over three positions, related by 3$_1$ screw axes.

Thermogravimetric analysis of {[Cu(4,4'-H$_2$dcbp)(SO$_4$)]·⅓H$_2$O} revealed a weight loss of 1.5% up to 100 °C, consistent with the loss of the guest water molecules. No further weight loss is observed until decomposition begins at 380 °C. Heating a single crystal of {[Cu(4,4'-H$_2$dcbp)(SO$_4$)]·⅓H$_2$O} at 150 °C for 2 hours, showed it to maintain crystallinity, suggesting the network is robust in the absence of water and to heat treatment. Furthermore, a crystal data collection performed on the heated crystal yielded almost identical cell parameters, although this time refined to be the desolvated structure [Cu(4,4'-H$_2$dcbp)(SO$_4$)] which displays the same 3D network. Unfortunately, the channels are inaccessible to any gases tested (H$_2$, CH$_4$, N$_2$, CO$_2$) suggesting that their diminished size restricts access to them.[22]

Variable temperature magnetic susceptibility measurements reveal very weak antiferromagnetic coupling between the Cu(II) centres within both the chloride and sulfate bridge species, $J = -3.02$ and -1.90 cm^{-1}, respectively.[22]

3.2 Coordination Polymers of 4,4'-H$_2$dcbp and Ba(II) and Sr(II) Metal Ions

Although, undoubtedly, control of main group metal-based frameworks in the construction of coordination polymers remains a challenge due to the metal ions' lack of preferred geometrical orientation and coordination number, they do offer the advantage of potentially producing structurally interesting and diverse materials with potentially interesting properties. Also, the oxophilic nature of these metal ions renders them ideal candidates for coordination with oxygen donor ligands such as 4,4'-H$_2$dcbp. In contrast to the transition metal ions, the main group metals have no predisposed coordination constraints. Within {[Ba(4,4'-dcbp)(H$_2$O)$_{0.4}$]·0.6H$_2$O} the metal centre is ten-coordinate with the 4,4'-dcbp ligand chelating *via* its bipyridyl nitrogen atoms, in addition to seven oxygen atoms from five carboxylate groups and one water molecule.[14] The 4,4'-dcbp ligand interacts with six Ba(II) centres, and likewise each Ba(II) centre interacts with six 4,4'-dcbp ligands to generate the neutral 3D coordination polymer. The 3D coordination network contains channels that run down the crystallographic *c* axis. In the underlying network both the Ba(II) atoms and 4,4'-dcbp ligands act as six-connecting nodes, each coordinating to six of the other nodes. The two nodes are topologically different, generating a binodal six-connected network with (4^9.6^6)(4^{10}.6^5) topology (Fig. 9).

Within {[Sr(4,4'-dcbp)]·H$_2$O} the metal centre is eight-coordinate with the
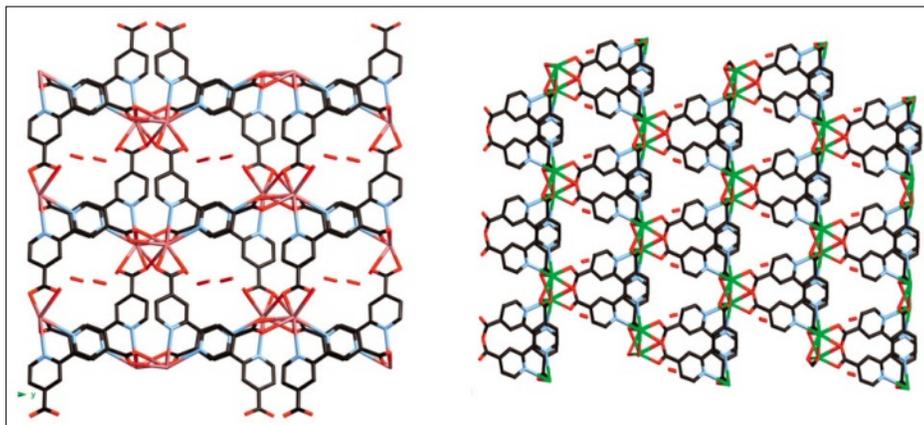
Fig. 9. The 3D network in {[Ba(4,4'-dcbp)(H₂O)₀.₄]·0.6H₂O} (left) and the 3D network in {[Sr(4,4'-dcbp)]·H₂O} (right) as viewed down their crystallographic *c*-axes showing the channels with lattice water molecules included. Adapted from ref. [14]. Reproduced by permission of the Royal Society of Chemistry.

4,4'-dcbp ligand chelating through its bipyridyl nitrogen atoms, and six carboxylate oxygen atoms from five adjacent 4,4'-dcbp ligands.[14] Each Sr(II) metal centre interacts with six 4,4'-dcbp ligands and likewise each 4,4'-dcbp ligand interacts with six Sr(II) centres to generate the neutral 3D coordination polymer (Fig. 9). This network contains channels that run down the crystallographic *c* axis and these channels account for 11% of the crystal volume. The polymer can be reduced to a six-connected network by assigning the Sr(II) atoms and 4,4'-dcbp ligands as nodes; each connects to six of the others. Although the two nodes are chemically different, in the idealised net all nodes are equivalent, and thus the Schläfli symbol for this uninodal six-connected network is $(4^9.6^6)$.

4. Coordination Polymers of 4,4',6,6'-H₄tcbp and Ba(II) and Representative Ln(III) Metal Ions

The 4,4',6,6'-H₄tcbp ligand should allow coordination of larger metal ions with higher stability within the 'expanded' tetradentate chelating site and in addition to the peripheral 4,4'-carboxylate groups. The structure of [Ba₂(4,4',6,6'-tcbp)(H₂O)₂] has two unique Ba(II) environments with Ba1 and Ba2 eight- and nine-coordinate, respectively.[14] The 4,4',6,6'-tcbp ligand chelates to Ba1 through its tetradentate bipyridyl-carboxylate core with four further oxygen atoms, from four adjacent carboxylate groups, completing its coordination sphere. Two water molecules along with seven carboxylate oxygen atoms from six adjacent 4,4',6,6'-tcbp ligands, coordinate Ba2. Each ligand interacts with eleven Ba(II) metals centres (five Ba1 centres and six Ba2 centres) and likewise each Ba1 and Ba2 metal centre interacts with five and six 4,4',6,6'-tcbp ligands, respectively. These interactions yield a very complicated

5,6,11-connected 3D polymeric network (Fig. 10).

Within the structure of {[La(4,4',6,6'-Htcbp)(H₂O)₃]·H₂O} the La(III) metal centre is nine-coordinate with one 4,4',6,6'-Htcbp ligand chelating in tetradentate fashion *via* two bipyridyl nitrogen atoms and the two 6,6'-carboxylate oxygen atoms.[23] Three-coordinated water ligands and two carboxylate oxygen atoms from two adjacent units complete the coordination sphere about La(III). The coordination of 4,4',6,6'-Htcbp is such that

Fig. 10. The highly connected metal-ligand environment in [Ba₂(4,4',6,6'-tcbp)(H₂O)₂]. Adapted from ref. [14]. Reproduced by permission of the Royal Society of Chemistry.
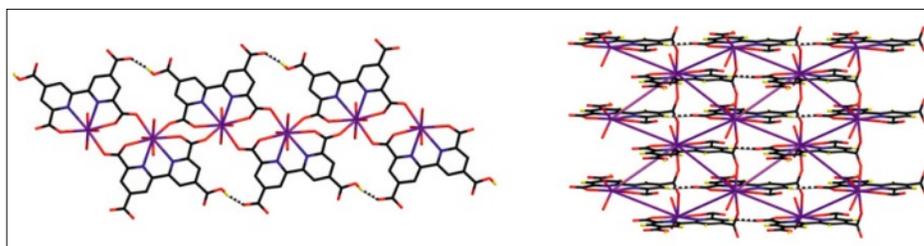
it interacts with three metal centres with the 6- and 6'-carboxylate groups bridging between them such that a 1D polymeric chain results (Fig. 11). Each chain is directly connected to six neighbouring chains through hydrogen bonding, resulting in a complicated 3D network.

Within the structures of {[Ln(4,4',6,6'-Htcbp)(H₂O)]·2H₂O} (where Ln = Eu or Gd) the 4,4',6,6'-Htcbp ligand coordinates to the Ln atom in a tetradentate fashion *via* two nitrogen atoms and the 6,6'-carboxylate oxygen atoms. The ligand then further coordinates to two other Ln atoms, each *via* the two oxygen atoms of a 4-carboxylate group, while the other 4'-carboxylic acid group does not coordinate and remains protonated. In turn, each Ln atom is coordinated to one tetradentate chelating 4,4',6,6'-Htcbp ligand and two other *trans*-disposed 4,4',6,6'-Htcbp ligands *via* peripheral carboxylate groups. The eight-coordinate geometry about the Ln-centre is completed by two *cis*-disposed, symmetry related water molecules. Each [Ln4,4',6,6'-Htcbp] moiety (node) is connected into 2D sheets with (4,4)-topology (Fig. 11).

Clearly the 4,4',6,6'-H₄tcbp ligand avidly coordinates to metal ions from across the main group and lanthanide series with a high degree of connectivity, however, this greater connectedness often comes at the expense of porosity. However, in related work we have shown that the self-assembly of the [Na₄(4,4',6,6'-tcbp)] ligand with various Ln(III) ions [Ln(III) = Eu, Nd, Gd, and Tb] yields a family of discrete isostructural {Na₂[Ln₂(4,4',6,6'-tcbp)₂]} complexes and permits sensitisation of the Ln(III) ions and the striking luminescence in water in either the visible or near-IR regions, despite their high hydration states.[24] These studies augur well for the potential formation of luminescent coordination polymers and studies of this nature form the basis of some of our ongoing work.

4.1 *Solvothermal in situ Ligand Reactivity: The Formation of 4,4',6-Tricarboxy-2,2'-bipyridine*

Solvothermal synthesis has typically become *de rigueur* in the formation of coordination polymers.[15] However, in some

Fig. 11. Polymer structure of {[La(4,4',6,6'-Htcbp)(H₂O)₃]·H₂O} showing the 1D chain (left) and the 2D structure of {[Ln(4,4',6,6'-Htcbp)(H₂O)]·2H₂O} showing the 2D sheet (right). The purple lines between the Ln atoms highlight the (4,4) topology formed by the [LnHtcbp] nodes. Adapted from ref. [23]. Reproduced by permission of the Royal Society of Chemistry.

instances a consequence of such forcing conditions is the occurrence of unexpected side reactions during solvothermal treatment although these can provide unique routes to useful ligands or engender decomposition pathways within ligand species. In work referred to above we developed a solvothermal oxidation protocol that employs dilute aqueous nitric acid solutions in the synthesis of the polypyridine polycarboxylic acid ligands from their methylprecursors. We then modified the approach by incorporating a Cu(II) ion in the oxidation solution to see whether a coordination polymer might be formed following (or during) the oxidation of the ligand precursor.[12] To this end we treated an aqueous nitric acid solution of 4,4',6,6'-tetramethyl-2,2'-bipyridine with Cu(II) ions under solvothermal conditions and successfully isolated a Cu(II) coordination polymer which was structurally characterised to identify {[Cu(HL')(H$_2$O)]·H$_2$O} containing the novel ligand 4,4',6-tricarboxy-2,2'-bipyridine. As can be seen from Fig. 12, it is immediately apparent that decarboxylation of 4,4',6,6'-H$_4$tcbp at the 6'-position to form a novel ligand has occurred: 4,4',6-tricarboxy-2,2'-bipyridine, HL'. This newly formed ligand is chelating to Cu(II) in tridentate fashion *via* the 2,2'-bipyridyl-6-carboxylate core. Coordination about the copper centre is completed by a water molecule and a symmetry related 4-carboxylate oxygen atom from a neighbouring unit that leads to the formation of a 1D polymeric chain. The 1D chains interact with one another, in the first instance, through strong hydrogen-bond interactions between the carboxylic acid oxygen atom and the carboxylate oxygen atom of an adjacent chain. The chains are further interconnected *via* the hydrogen bond donor/acceptor functionality provided by the aqua ligand, which interacts with non-coordinating carboxylate from an adjacent chain. On the basis of these interactions, the structure is best described as a series of one-dimensional coordination polymer chains engaged in three-dimensional hydrogen bonding interactions, in which each one-dimensional chain is directly linked to four others through the hydrogen bond donors and acceptors present on the [Cu(HL')(OH$_2$)] unit, and each lattice water molecule links a further three chains.

In situ solvothermal ligand reactions offer a fascinating route to the formation of new ligand types that may not be necessarily easily synthesised through more traditional methods. Indeed, the serendipitous formation of 4,4',6-tricarboxy-2,2'-bipyridine through decarboxylation offers a potential viable route to its formation. These results have demonstrated the importance of careful control of reaction conditions in the solvothermal synthesis of coordination
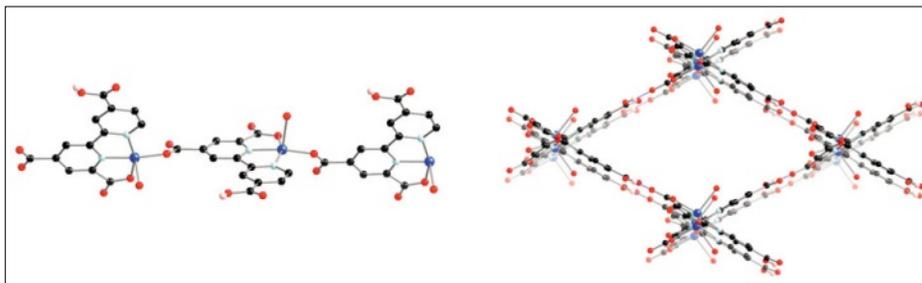
Fig. 12. The 1D polymer formed by {[Cu(HL')(H$_2$O)]·H$_2$O} (left) and part of the 3D network structure formed by hydrogen-bonding between adjacent 1D polymers (right). Adapted from ref. [12]. Reproduced by permission of Elsevier.
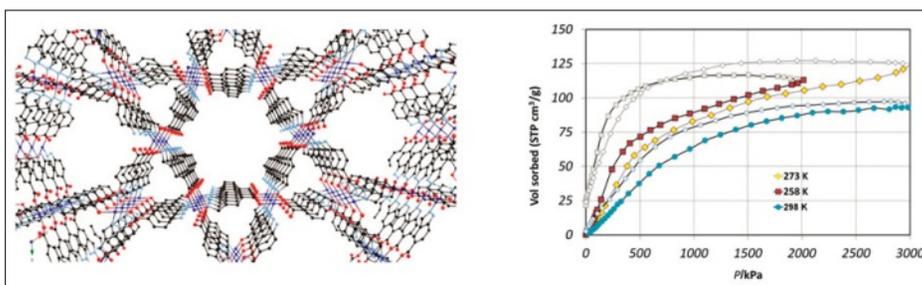
Fig. 13. The interpenetrated 3D network of [Cu(*1H*-indazole-5-carboxylate)] showing 1D channels (left) and the isotherms for CO$_2$ sorption for **1** at 258 K (red squares), 273 K (yellow diamonds) and 298 K (blue circles). The desorption isotherms are indicated by unfilled squares, diamonds and circles. Adapted from ref. [26]. Reproduced by permission of the Royal Society of Chemistry.

polymers, especially when employing the harshly oxidising environments typical of solvothermal techniques.

5. Conclusions, Current and Future Studies

Clearly we have shown that the 2,2'-bipyridine-poly-carboxylate family of ligands displays an array of different coordination abilities in the formation of coordination polymers with many interesting and varied properties. Whilst the polymers formed with 4,4'-dicarboxy-2,2'-bipyridine and 4,4',6,6'-tetracarboxy-2,2'-bipyridine are topologically very interesting, their high degree of connectedness often leads to the formation of dense crystalline phases that possess limited voids or channels within which to sorb other smaller molecules. We have begun to circumvent these issues by using 2,2'-bipyridine-poly-carboxylate ligands such as 4,4'-([2,2'-bipyridine]-4,4'-diyl)bis-benzoic acid where the distance between the 2,2'-bipyridine coordination site and the carboxylate coordination site is increased, offering a greater reach between metal centres and the advent of larger pores.[25] Results from this work are promising and will be reported in due course.

Another avenue of research that has derived from this work is the synthesis and discovery of new ligand types and their incorporation into coordination polymers. We have had recent success by moving to a different heterocyclic scaffold based upon indazole-carboxylates such as *1H*-indazole-5-carboxylic acid (H$_2$L).[26] This ligand retains the rigidity and coordinative ability of the heterocyclic scaffold as found in the 2,2'-bipyridine-poly-carboxylates but now has greater distance between the two coordinating functionalities which allows for the formation of frameworks with accessible pores. Briefly, Cu(HL)$_2$] is a thermally and hydrolytically robust four-connected 3D coordination polymer of NbO topology and is replete with 1D channels that permit selective (over N$_2$, H$_2$ and CH$_4$) and hysteretic sorption of CO$_2$ (24% by weight) (Fig. 13). Clearly, making subtle variations to this ligand scaffold augurs well for the formation and discovery of new coordination polymer types with potential porosity and promising sorption behaviour.[26]

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