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Synthesis, crystal structure and luminescent behaviour of coordination complexes of copper with bi- and tridentate amines and phosphonic acids

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ABSTRACT

The synthesis and crystal structure of four new copper(I) and copper(II) supramolecular amine, and amine phosphonate, complexes is reported. Reaction of copper(I) with 2-,9-dimethyl-1-10-phenanthroline (*dmp*) produced a stable 4-coordinate Cu(1) species, $[Cu^{(1)}(dmp)_2]Cl$ MeOH 5H₂O (2), i.e., the increased steric hindrance in the 'bite' area of *dmp* did not prevent interaction with the metal and provided protection against oxidation which was not possible for the phen analogue [R. Clarke, K. Latham, C. Rix, M. Hobday, J. White, CrystEngCommun. 7(3) (2005), 28-36]. Subsequent addition of phenylphosphonic acid to (2) produced two structures from alternative synthetic routes. An 'in situ' process yielded red block Cu(I) crystals, $[Cu^{(I)}(dmp)_2] \cdot [C_6H_5PO_3H_2 \cdot C_6H_5PO_3H]$ (4), whilst recrystallisation of (2) prior to addition of the acid ('stepwise' process) produced a green, needle-like Cu(II) complex, $[Cu^{(II)}(dmp) \cdot (H_2O)_2 \cdot C_6H_5PO_2(OH)] [C_6H_5PO_2(OH)] (3).$ However, addition of excess dmp during the 'stepwise' process forced the equilibrium towards product (4) and resulted in an optimum yield (99%). The structure of (4) was similar to the *phen* analogue, $[Cu^{(1)}Cl(phen)_2] \cdot [C_6H_5PO_2(OH) \cdot C_6H_5PO(OH)_2]$ (1) [R. Clarke, K. Latham, C. Rix, M. Hobday, J. White, CrystEngCommun. 7(3) (2005), 28-36], but the presence of dmp exerted some influence on global packing, whilst (3) exists as a polymeric layered material. In contrast, reaction of copper(I) with di-2-pyridyl ketone (dpk), followed by phenylphosphonic acid produced purple/blue Cu(II) species, $[Cu^{(II)}(dpk + H_2O)_2] Cl_2 + 4H_2O$ (5), and $[Cu^{(II)}(dpk + H_2O)_2] + [C_6H_5PO_2(OH)_2 + 2H_2O] Cl_2 + 4H_2O$ (5), and $[Cu^{(II)}(dpk + H_2O)_2] + [C_6H_5PO_2(OH)_2 + 2H_2O] Cl_2 + 4H_2O$ (5), and $[Cu^{(II)}(dpk + H_2O)_2] + [C_6H_5PO_2(OH)_2 + 2H_2O] Cl_2 + 4H_2O$ (5), and $[Cu^{(II)}(dpk + H_2O)_2] + [C_6H_5PO_2(OH)_2 + 2H_2O] Cl_2 + 4H_2O$ (5), and $[Cu^{(II)}(dpk + H_2O)_2] + [C_6H_5PO_2(OH)_2 + 2H_2O] Cl_2 + 4H_2O] Cl_2 + 4H_2O$ (5), and $[Cu^{(II)}(dpk + H_2O)_2] + [C_6H_5PO_2(OH)_2 + 2H_2O] Cl_2 + 4H_2O] Cl_2$ $C_{6}H_{5}PO(OH)_{2}$ (6), respectively, i.e., in both cases oxidation of copper occurred. Solid-state luminescence was observed in (2) and (4). The latter showing a 5-fold enhancement in intensity.

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1. Introduction

One of the lesser studied functionalities in crystal engineering is the phosphonate group (R–P(O)(OH)₂). Like sulphonic acids, phosphonic acids are strong acids, with the first pKa \approx 1–2, and so they remain ionised over a wide pH range in aqueous media. Each phosphonic acid group can provide one-, two- or three-oxygen atoms to coordinate metal ions, and thus the principal uses of these acids include chelation, e.g., to remove heavy metals from bleaching solutions in the paper, pulp and textile industry, and also scale inhibition [1]. Another fertile area of research has been the development of metal phosphonates, a class of organic-inorganic hybrid materials with a wide range of applications encompassing ion-exchange, intercalation, catalysis, light-harvesting, and molecular magnetic devices [2]. Phosphonic acids also form extremely strong hydrogen bonds. However, the rapid growth of metal phosphonates has overshadowed the potential of phosphonic acids to form supramolecular arrays.

Structural studies on phosphonate groups, with the aim of designing organic solids, have only recently been reported in the literature. These studies have examined only a small selection of acids, principally phenylphosphonic acid $[C_6H_5PO(OH)_2]$ [3–5], and those acids that have multiple functionalities and may form zwitterions, e.g., *N*-nitrilotri(methylphosphonic) acid, NTMP [6–8]. Some work has also been carried out on diphosphonic acids [9]. Deprotonation of organophosphonic acids, by amines (e.g., aniline, phenanthrolines, etc.) [3–7] or metal(II) salts (e.g., Mn, Co, Cu, Ni, Zn, Cd and mixtures of these ions) [3,4,8], appears to trigger a self-assembly process and lead to the formation of structurally robust and predictable aggregates.

We have reported a number of studies on the synthesis of copper(II)amine arylphosphonates with supramolecular architecture. These materials have the general formula: $[Cu^{II}(phen)_2X][((O-H)_2OPC_6H_5)]((OH)O_2PC_6H_5)]$ (where X = I, Br, Cl (1), NCS), and contain a 5-coordinate copper(II) cation, counterbalanced by a hydrogen-bonded phenylphosphonic acid dimer anion [4]. The complexes are associated through hydrogen bonding interactions between the phosphonic acids, and π - π interactions between *phen-phen, phen-acid*, and *acid-acid* aromatic rings. The supramo-



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lecular motifs observed in these systems are quite robust, and relatively unaffected by changes in X and the nature and position (o-, m- or p-) of substituents on the aromatic ring of the acid [10].

The aims of the present study were to synthesise analogues of $[Cu^{(II)}(phen)_2Cl][((OH)_2OPC_6H_5) ((OH)O_2P_6H_5)]$ (1), containing different amine species, and to explore the impact of this change on the oxidation state and coordination of the copper atom. Their affect upon local and global structure was also of considerable interest. The synthesis of the phen analogue (1) proceeds via a Cu(I) intermediate. However on addition of phenylphosphonic acid to $[Cu^{(I)}(phen)_2]X$ (X = Cl⁻, Br⁻) spontaneous oxidation to Cu(II), to produce $[Cu^{(II)}(phen)_2Cl][((OH)_2OPC_6H_5) ((OH)O_2P_6H_5)]$ (1) occurs [4]. This change in oxidation state has a number of chemical and physical consequences. For example, Cu(II) d⁹ typically exhibits 5- or 6-coordinate geometry, whilst Cu(I) d¹⁰ prefers 4-coordinate geometry [11] and when coordinated with two phen ligands, a square planar structure is observed [11]. The filled d¹⁰ orbital shell present in Cu(I) also participates in metal-to-ligand charge-transfer (MLCT), and on excitation, Cu(I) donates electrons to ligands, such as phen and its derivatives, and photoluminescence can be observed [12-14]. For example, Blaskie and McMillin [12] observed photoluminescence lasting 54 ns at ambient temperatures for $[Cu^{(1)}(dmp)_2]^+$ in dichloroethane. Hence, it would be beneficial to have some control on the oxidation state and geometry exhibited by these species, in order to exploit potential applications in sensor design and/or redox capability. The amines used in this study are shown in Fig. 1.

The *phen* ligand, as a planar and rigid amine with aromatic π electrons, is an excellent candidate for the engineering of structures, but does leave the Cu(I) centre exposed to oxidation. Thus, 2,9-dimethyl-1,10-phenanthroline (*dmp*), with slightly bulky substituents in the 2- and 9-positions, was selected since this ligand may protect the Cu(I) centre from oxidation, or at least enforce a tetrahedral geometry on the metal – a geometry generally much more favourable for Cu(I) than Cu(II). However, it should not be too large to prevent intercalation into the voids between the phenylphosphonate layers, although it may alter some of the packing characteristics.

The related ligand, di-2-pyridylketone (*dpk*), is an excellent candidate for metal-complex extended-structure systems [15], and can behave as either a bidentate or tridentate ligand [15], commonly chelating through *N*,*N* or *N*,*O* coordination [15–17]. However, it is also capable of *N*,*N*,*O* chelation after hydration of the ketocarbonyl group, to form a *gem-diol*, represented as (*dpk* · H₂O), which may ionise to yield a monoanionic ligand (Fig. 2) – a reaction which is known to be promoted by metal ion coordination [15]. *Dpk* has not been investigated in a crystal engineering capacity when coordinated with copper and phenylphosphonic acid.

In this work, studies were performed to compare the stability, coordination and crystal structure of the Cu(I)/Cu(II) complexes of *dpk*, with those of *phen* and *dmp* analogues, to gain insight into the effect of using a sterically 'open' ligand with potential triden-

tate character, and functional groups (C=O/C-OH) that may engage in additional H-bonding interactions.

2. Experimental

2.1. Materials

Copper(I) chloride was prepared according to published procedures [18]. Phenylphosphonic acid (98%), 2,9-dimethyl-1,10-phenanthroline (*dmp*) (98%), and di-2-pyridylketone (*dpk*) (99%) were all obtained from Aldrich Chemicals, and used without further purification.

2.2. Physical measurements

Fourier transform infrared spectra (4000–400 cm⁻¹) of the complexes were recorded on a Perkin Elmer 1725X spectrometer as KBr disks. Powder xrd spectra, of the powdered, homogeneous bulk material, were collected on a Bruker D8 ADVANCE diffractometer using graphite-monochromated Cu K α radiation (λ = 1.5406 Å): scan range 3–60° 2 θ , step size 0.02°, count rate 2 s. Spectra were compared to powder spectra generated from single crystal data using Mercury software [22]. Elemental analysis for C, H, N, P and Cl was performed by the Campbell Microanalytical Laboratory at the University of Otago, New Zealand.

Fluorescence measurements were carried out using a Fluorolog-3 fluorescence spectrometer from Jobin–Yvon–Horiba fitted with a 450 W Xe lamp. The powdered samples were loaded evenly into the sample cavity of the solid sample holder and the fluorescence emission spectra were collected between 450 and 750 nm, at an angle 45° to the incident beam, using an excitation wavelength of 400 nm, and a slit width of 1 nm. All spectra were collected at room temperature.

2.3. Synthesis of the complexes

2.3.1. [Cu⁽¹⁾(dmp)₂]Cl · MeOH · 5H₂O (2)

A degassed suspension of 2,9-dimethyl-1,10-phenanthroline (dmp) (0.915 g, 0.0051 mol, 30 mL ethanol) was added to copper(I)chloride (0.2 g, 0.0020 mol, 20 mL ethanol) giving a darkred solution. This solution was stirred for 3 h at room temperature in a two-neck round-bottomed flask, fitted with a condenser and N₂ gas flush. The reaction mixture was filtered to remove any solid impurities, and the solvent removed from the red/orange filtrate using a rotary evaporator. The remaining solid was recrystallised from a 1:1 aqueous methanol solution. Crystals were collected and washed with a few drops of cold Milli-Q water, giving red/orange, fine needle crystals, which slowly became brown as the crystals desolvated. Suitable X-ray diffraction quality single crystals were isolated mechanically from the bulk material. Yield 55%. *Anal.* Calc. for [C₂₈H₂₄N₄CuCl]: C, 65.24; H, 4.69; N, 10.87; Cl, 6.88. Found: C, 63.04, H, 5.04, N, 10.57, Cl, 6.79%.



Fig. 1. (a) 1,10-Phenanthroline and its derivatives and (b) di-2-pyridyl ketone (dpk).



Fig. 2. The hydration of dpk [17].

2.3.2. $[Cu^{(II)}(dmp) \cdot (H_2O)_2 \cdot C_6H_5PO_2(OH)]^+ [C_6H_5PO_2(OH)]^- (\mathbf{3}) -$ 'stepwise' technique (Scheme 1)

Crystals of $[Cu^{(1)}(dmp)_2]^+Cl^- \cdot MeOH \cdot 5H_2O$ (**2**) were dissolved in ethanol (0.32 g, 15 mL), and the solution added to an ethanolic solution of phenylphosphonic acid (0.2 g, 0.0012 mol, 20 mL). The reaction mixture was then stirred for 2 h, under N₂, and filtered to remove any solid impurities. The filtrate was then evaporated under vacuum, with the remaining solid (a mixture of red and green microcrystals) recrystallised twice from a 1:1 ethanol/water solution. Green shard-like crystals were obtained. Suitable X-ray diffraction quality single crystals were isolated mechanically from the bulk material. Yield 29%. *Anal.* Calc. for $[C_{26}H_{28}N_2O_8P_2Cu]$: C, 50.21; H, 4.54; N, 4.50; P, 9.96. Found: C, 50.53; H, 4.75; N, 4.55; P, 9.72%.

2.3.3. $[Cu^{(l)}(dmp)_2]^* \cdot [C_6H_5PO_3H_2 \cdot C_6H_5PO_3H]^-$ (**4**) – 'in situ' technique (Scheme 1)

A degassed suspension of *dmp* (2.265 g, 0.013 mol, 30 mL ethanol) was added to copper(1)chloride (0.495 g, 0.005 mol) giving a dark-red solution. This solution was stirred under N₂ in a two neck flask fitted with a condenser, for 2 h at room temperature. A phenylphosphonic acid solution (1.268 g, 0.004 mol, 30 mL ethanol) was then added to the suspension and stirring continued for a further two hours under N₂. The red/orange solution was filtered to remove any solid impurities. Red block crystals were obtained by ether diffusion into the filtrate. Suitable X-ray diffraction quality single crystals were isolated mechanically from the bulk material. Yield 33%. *Anal.* Calc. for $[C_{40}H_{37}N_4O_6P_2Cu]$: C, 60.41; H, 4.69; N, 7.05; P, 7.79. Found: C, 59.39; H, 4.84; N, 6.98; P, 7.51%.

2.3.4. $[Cu^{(1)}(dmp)_2]^+ \cdot [C_6H_5PO_3H_2 \cdot C_6H_5PO_3H]^-$ (**4a**) – 'ligand addition' technique (Scheme 1)

An excess of *dmp* ligand (0.1224 g, 0.0006 mol) was added to an ethanolic solution of $[Cu^{(1)}(dmp)_2]^+Cl^- \cdot MeOH \cdot 5H_2O$ (**2**) (0.32 g, 0.0006 mol, 15 mL), and stirred for 10 min. This solution was then added to an ethanolic solution of phenylphosphonic acid (0.2 g, 0.0012 mol, 20 mL), and the mixture stirred for 2 h under N₂, and then filtered to remove any solid impurities. The crimson coloured filtrate was then evaporated to dryness and the remaining solid recrystallised from a 1:1 aqueous ethanol solution. Red block crystals grew within 2 weeks. Yield 99%. *Anal. Calc.* for $[C_{40}H_{37}N_4O_6P_2^-$

Cu]: C, 60.41; H, 4.69; N, 7.05; P, 7.79. Found: C, 59.85; H, 4.60 N; 6.96; P, 7.73%.

2.3.5. $[Cu^{(II)}(dpk \cdot H_2O)_2] \cdot 2Cl \cdot 4H_2O(5)$

A degassed solution of di-2-pyridylketone (*dpk*) (0.459 g, 0.00255 mol, 10 mL ethanol) was added to a suspension of copper(l)chloride (0.1 g, 0.0010 mol, 20 mL ethanol) giving a dark red/brown solution. This suspension was stirred for approximately 2 h at room temperature under N₂. The reaction mixture, now a brilliant blue colour, was filtered to remove any solid impurities. The filtrate was evaporated using a rotary evaporator and the remaining solid recrystallised from a hot 1:1 aqueous/ethanol solution. Blue/purple block – like crystals were formed. Suitable X-ray diffraction quality single crystals were isolated mechanically from the bulk material. Yield 54%. *Anal.* Calc. for [$C_{22}H_{20}N_4O_4CuCl$]: C, 52.49; H, 4.00; N, 11.13; Cl, 7.04. Found: C, 52.01; H, 3.97; N, 11.37; Cl, 6.95%.

2.3.6. $[Cu^{(II)}(dpk \cdot H_2O)_2] \cdot [C_6H_5PO_2(OH)]_2 \cdot [C_6H_5PO(OH)_2]$ (**6**) – 'ligand addition'-technique

Crystals of $[Cu^{(II)}(dpk \cdot H_2O)_2 \cdot 2Cl^- \cdot 4H_2O]$ (5) (0.11 g, 0.00021 mol) were dissolved in warm methanol (20 mL). Additional *dpk* (0.06 g 0.00033 mol) was added and stirred in the warm solution for 30 min. Phenylphosphonic acid (0.07 g, 0.00044 mol) was then added to the solution, stirred for 2 h, filtered to remove any undissolved material, and allowed to crystallise. Purple clustered crystals were obtained between 1 and 3 weeks. Suitable X-ray diffraction quality single crystals were isolated mechanically from the bulk material. Yield 48%. *Anal.* Calc. for $[C_{40}H_{39}N_4O_{13}P_3-Cu]$: C, 52.35; H, 3.87; N, 7.18; P, 7.94. Found: C, 52.04; H, 4.12; N, 7.01; P, 7.55%.

2.3.7. $[Cu^{(II)}(dpk \cdot H_2O)_2] \cdot [C_6H_5PO_2(OH)]_2 \cdot [C_6H_5PO(OH)_2]$ (**6a**) – 'in situ' technique

A solution of *dpk* (0.46 g, 0.00255 mol, 15 mL ethanol) was added to a suspension of copper(I) chloride (0.1 g, 0.0010 mol, 10 mL ethanol) giving a dark red/brown solution. This solution was stirred in a round-bottomed flask for 1 h. Phenylphosphonic acid (0.16 g, 0.001 mol) was then added to this solution, and the reaction mixture stirred for a further 2 h. After 5 days a purple powder was filtered from the reaction mixture. Yield 43%. *Anal.* Calc. for $[C_{40}H_{39}N_4O_{13}P_3Cu]$: C, 52.35; H, 3.87; N, 7.18; P, 7.94; Cu, 8.15. Found: C, 51.46; H, 4.68; N, 6.81; P, 7.25; Cu, 7.99%.

2.4. Crystal structure determination

In the present study, the structures of products (2-4) and (6) were determined and analysed for the first time by single crystal X-ray diffraction. Products (1) and (5) have been previously reported (CCDC No. 216752 [4] and BPYKTA10 [17], respectively). Crystal data were collected at 130 K for all structures, using graphite monochromated Mo Ka radiation for compounds (2-4) and Cu Kα radiation for (**5**) and (**6**). Data for (**5**) and (**6**) were collected and integrated using an Oxford Enhance system, whilst for compounds (2-4) the data were collected and integrated using a Bruker SMART CCD area detector system. In all cases, structures were solved by direct methods, using SHELXS-97 [19] (5) and (6) or SHELXTL [20] (2-4), and refined using SHELXL-97 [19] (5) and (6) or SHELXTL [20] (2-4). A mixed strategy was used for the refinement of hydrogen atoms. Hydrogen atoms attached to carbon were placed in calculated positions with a C-H distance of 0.93 Å, whilst hydrogen atoms attached to oxygen were located from difference Fourier maps, and refined without constraint. Molecular graphics were performed using ZORTEP [21], SHELXTL [20] and Mercury [22] programs. Selected crystal data are displayed in Table 1.

Table 1										
Summary	single	crystal	xrd	data	for	compounds	(1)) to	(6)	

	(1) [4]	(2)	(3)	(4)	(5)	(6)
Empirical formula	C36H29ClCuN4O6P2	C29H38ClCuN4O6	C26H28CuN2O8P2	C40H37CuN4O6P2	C22H28Cl2CuN4O8	C40H42CuN4O13
Molecular weight	774.56	637.62	621.98	795.22	610.92	940.20
Crystal class	monoclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space, group	C2/c	ΡĪ	P2(1)/c	ΡĪ	C2/c	C2/c
a (Å)	25.057(3)	6.996 (2)	13.5560(12)	10.8687(8)	14.46510(10)	37.7383
b (Å)	8.3700(10)	15.307 (5)	10.5757(10)	13.3371(10)	12.19030 (10)	11.4540(9)
c (Å)	16.546(3)	15.667(5)	18.7833(17)	13.9517(11)	14.53140(10)	23.3422(17)
α (°)	90.00	65.22	90.00	107.5840(10)	90.00	90.00
β (°)	103.370(10)	83.03	107.155(2)	102.0590(10)	90.8620(10)	125.325(1)
γ.(°)	90.00	87.65	90.00	97.5280(10)	90.00	90.00
$V(\dot{A}^3)$	3376.1(8)	1511.86	2573.0(4)	1844.0(2)	2562.09(3)	8232.0(11)
Ζ	4	2	4	2	4	8
Crystal, colour	block, blue	rod, red	slab, green	block, red	block, purple	block, purple
Crystal size (mm)	$0.65 \times 0.54 \times 0.25$	$0.1 \times 0.15 \times 0.45$	$0.1 \times 0.40 \times 0.40$	$0.25 \times 0.40 \times 0.45$	$0.35 \times 0.33 \times 0.26$	$0.35 \times 0.40 \times 0.40$
Temperature (K)	293(2)	130 (2)	130(2)	130(2)	130(2)	130(2)
Rad wavelength (Å)	0.71069	0.71073	0.71073	0.71073	1.54184	1.54184
Radiation type	Μο Κα	Μο Κα	Μο Κα	Μο Κα	Cu Kα	Cu Kα
θ minimum-maximum (°)	2.53-24.98	1.57-25.00	1.57-27.53	1.59-27.52	5.61-66.00	1.75-25.00
Index ranges	$0 \leqslant h \geqslant 29$	$-8 \leqslant h \geqslant 8$	$-16 \leq h \geq 17$	$-12 \leqslant h \geqslant 14$	$-17 \leqslant h \geqslant 17$	$-44 \leqslant h \geqslant 43$
	$0 \leqslant k \geqslant 9$	$-17 \leqslant k \geqslant 18$	$-13 \leqslant k \geqslant 12$	$-17 \leqslant k \geqslant 17$	$-14 \leqslant k \geqslant 13$	$-13 \leqslant k \geqslant 7$
	$-19 \leqslant l \geqslant 19$	$-14 \leqslant l \geqslant 18$	$-17 \leqslant l \geqslant 24$	$-15 \leqslant l \geqslant 18$	$-17 \leq l \geq 17$	$-27 \leqslant l \geqslant 27$
Number of reflections	2947	5233	5844	8083	2109	7260
$R_1 (F^2 > 2\sigma (F^2))$	0.0375	0.0626	0.0425	0.0475	0.0374	0.0612
$wR(F^2)$	0.1028	0.1833	0.0992	0.1179	0.0978	0.01662
S	1.074	1.019	1.028	1.043	1.177	1.053

3. Results and discussion

3.1. Phenanthroline derivatives

The reaction of copper(I) chloride with a methanolic solution of *dmp*, using the method of Pallenberg et al. [14] produced red, needle-like crystals. Elemental analysis indicated a 1:2:1 molar ratio of Cu:dmp:Cl, in agreement with the empirical formula, $[Cu^{(1)}(dmp)_2]Cl \cdot MeOH \cdot 5H_2O$ (2). Addition of phenylphosphonic acid to an ethanolic solution of recrystallised (2), henceforth known as the 'stepwise route' (Scheme 1), yielded a mixture of red (Cu(I)) and green (Cu(II)) crystals. The green, needle-like crystals (3), were separated from the red crystals by aqueous extraction, and were found to contain a copper:phosphorus:water:*dmp* ratio of 1:2:2:1 and an empirical formula, [Cu^(II)(*dmp*). $(H_2O)_2 \cdot (C_6H_5PO_2(OH))_2$] (3). No chloride was present, and the 5coordinate Cu(II) species was bonded to a single *dmp* ligand, i.e. a composition rather different to the *phen* analogue (1) [4]. Therefore, using this 'stepwise' approach - isolation of (2) prior to the addition of acid - the Cu(I) state was not retained, and addition of acid resulted in both oxidation of the metal and cleavage of a dmp ligand. Due to the poor yield and quality of the red crystalline product, precise structural identification was not possible. However, preliminary analysis suggested that this could be starting material (2).

An alternative, '*in situ*' route (Scheme 1): direct addition of phenylphosphonic acid to a copper(I) chloride – *dmp* reaction mixture without isolation and purification of (**2**), produced red block-crystals with a Cu:P:*dmp* ratio of 1:2:2. The red colour indicated that the +1 oxidation state of copper had been retained on addition of the acid, and that the crowding effect of the methyl groups on the *dmp* could prevent oxidation of the metal centre, if this route was followed. Thus, displacement of one of the *dmp* ligands did not occur using the '*in situ*' technique, and a composition very similar to (**1**) [4], except for the absence of chloride and the presence of monovalent copper, was obtained.

It was hypothesised that cleavage of one of the bidentate *dmp* ligands, which occurs in the '*stepwise*' route during reaction with phenylphosphonic acid, may be due to the presence of excess acid

or, alternatively, a deficit of *dmp* in the reaction mixture, and therefore this displacement may be prevented if the excess was countered. A one mole excess of *dmp* was added to the isolated intermediate (**2**) prior to reaction with phenylphosphonic acid ('*ligand addition route*' – Scheme 1). Red block-shaped crystals (**4a**), similar in appearance and composition to (**4**) were obtained. Furthermore, the addition of excess *dmp* pushed the reaction almost to completion, and resulted in a 99% yield.

3.2. FT-IR spectroscopy

The solid-state Fourier transform infrared spectra of all complexes were fully consistent with their single crystal structures with the structural differences between the 'stepwise' (3) and ' in situ' (4) compounds readily observed (Table 1). The most obvious variation, a broad band at approximately 3424 cm⁻¹ in the 'stepwise' complex, $[Cu(dmp) \cdot (H_2O)_2 \cdot C_6H_5PO_2(OH)]^+[C_6H_5PO_2(OH)]^-$ (3) was attributed to the v(O-H) stretch of the coordinated water molecules. The 'in situ' $[Cu(dmp)_2]^+ \cdot [C_6H_5PO_3H_2 \cdot C_6H_5PO_3H]^$ product (4) does not possess water molecules and therefore does not show this feature in its IR spectrum. The IR spectra also support the presence of phenylphosphonate anions and *dmp*. Corresponding v(PO-H) stretches at approximately 2400 cm⁻¹ are present in the spectra of both (3) and (4), together with the classic PO₃ vibrations at 1138, 1080, 1040 and 926 cm⁻¹ (typically 1200-900 cm⁻¹). The presence of *dmp* was revealed by bands at around 1625, 1590 and 860 cm⁻¹, which are consistent with amine ligands coordinated to a copper ion. Bands observed in both the IR spectra of the 'in situ' and 'ligand addition' complexes, are almost identical in frequency and in relative intensity, thus confirming that these two products are very similar. For spectra and tables of FTIR data please see Supplementary material.

3.3. Powder XRD

All experimental powder spectra (**2–4a**) show excellent pattern matching to the powder spectra generated from the single crystal data using Mercury [22]. Thus we can conclude that the composition and structure of the bulk are the same as the isolated single



Scheme 1.

crystals in each case. Spectra were in general of a high quality, showing well-resolved peaks, with the exception of the powder XRD pattern of the '*stepwise*' product (**3**) which contains some amorphous material, as indicated by the broad peak in the region $9-15^{\circ} 2\theta$. The spectra of the '*in situ*' (**4**) and the '*ligand addition*' (**4a**) crystal products are very similar, see Supplementary material for spectra and tables of xrd data.

Thus from FT-IR and powder xrd data we can confirm that products (**4**) and (**4a**) are indeed the same, and that both oxidation of the copper(I) centre, and cleavage of one of the *dmp* ligands, can be prevented by addition of excess *dmp* during the '*stepwise*' route.

3.4. Solid-state luminescence in phenanthroline derivatives

The solid-state luminescence spectrum of bis(*dmp*)copper(I) chloride (**2**) showed a single (FWHM ~ 150 nm) strong emission band at ~730 nm when excited at 400 nm. The copper(I) *dmp* phenylphosphonate derivative (**4**) exhibited a similar emission band at ~730 nm, with a similar FWHM, but with a 5-fold enhancement in intensity, which was attributed to the extended π -system present in the phosphonate supramolecular assembly.

3.5. Di-2-pyridylketone (dpk) derivatives

3.5.1. Synthesis of copper-dpk intermediate (5)

The isolation of a copper-dpk intermediate was attempted using the same molar ratio (1:2.5) of copper:dpk as used in the dmp synthesis (**2**). Blue/purple block crystals of (**5**) were obtained,

with the colour providing convincing evidence of a Cu(II) species. Thus, like the *phen* analogue (1) [4], the open nature of the ligand does not inhibit oxidation of the copper centre. Elemental analysis indicated a 1:2:2 molar ratio of Cu:*dpk*:Cl, in agreement with the empirical formula, $[Cu^{(II)}(dpk)_2]Cl_2 \cdot 4H_2O$ (5).

As in the *dmp* experiments, addition of phenylphosphonic acid to (**5**) was attempted via both the '*in situ*' and '*ligand addition*' synthetic procedures (Scheme 1). The '*ligand addition*' synthesis produced purple, rod-like crystals (**6**) with a Cu:P:*dpk* ratio of 1:3:2, whilst the '*in situ*' synthesis yielded a purple powder (**6a**). In the latter case, the product was not of sufficient quality to perform single crystal X-ray diffraction analysis, but elemental analysis was consistent with the presence of two *dpk* ligands, as well as the existence of phenylphosphonate acid in the complex, i.e., (**6a**) has a similar molecular composition to (**6**).

3.5.2. FT-IR Spectroscopy

A significant feature in the infra-red spectrum of (**5**), (**6**) and (**6a**) is that the strong carbonyl band at 1683 cm⁻¹ present in the free *dpk* ligand has been replaced by a strong band at around 3172 cm⁻¹ corresponding to an v(O-H) stretch. This is attributed to the well established hydration of the *dpk* ligand. Relevant literature [15,16] also indicates that the bands at 1469 cm⁻¹ and 1444 cm⁻¹ in (**5**) are also characteristic of $[M(dpk \cdot H_2O)_2]^{2+}$ cations. Therefore all three complexes contain *dpk* in the *gem-diol* form.

The same vibrations occur in the spectrum of (**6**), but are slightly shifted (3435 cm⁻¹ (ν (O–H)), 1607 cm⁻¹, 1469 cm⁻¹,

1446 cm⁻¹), together with a group at 671–628 cm⁻¹ also present in the spectrum of (**5**). Characteristic stretches of phenylphosphonate, are also observed, most notably the distinguishing series of PO_3 bands in the range of 1200–900 cm⁻¹. The FTIR spectra of (**6**) and (**6a**) are very similar, thus the '*ligand addition*' and '*in situ*' routes have resulted in materials with very similar compositions and structures.

3.5.3. Powder XRD

The powder X-ray diffraction spectrum of the '*in situ*' product (**6a**) is similar to the powder spectrum generated by Mercury [22] from the single crystal data of (**6**), but there are some discrepancies. Thus (**6**) and (**6a**) may not be identical, and the structure of the latter cannot be completely solved at present.

3.6. Crystal description

3.6.1. Structures of compounds (**2–4**) – phenanthroline derivatives

а

The structure of the copper–*dmp* intermediate was confirmed by single crystal *x*rd (Fig. 3a). The molecular unit contains a 4-coor-

dinate $[Cu^{(1)}(dmp)_2]^+$ cation, counter-balanced by a chloride anion, with one methanol and five water molecules completing the unit $([Cu^{(1)}(dmp)_2]Cl \cdot MeOH \cdot 5H_2O$ (**2**)). The closest relative to this structure is the perchlorate analogue, $[Cu^{(1)}(dmp)_2]ClO_4$, reported by Dessy and Fares [23], though the former is monoclinic, space group $P2_1/n$, whilst (**2**) is triclinic $P\overline{1}$.

As illustrated, the copper bonds to four nitrogen atoms of two *dmp* molecules. These Cu–N bonds (Tables 2 and 3) are unsymmetrical, as is the case in the perchlorate [23] and other copper–*dmp* complexes [26], resulting in a distorted tetrahedral structure with the two *dmp* ligands on different planes in order to minimise steric repulsion between the methyl groups (74° angle between planes). The charge-balancing chloride anion is disordered over two positions (occupancies Cl and Cl', 0.522 and 0.478, respectively).

The complex exists as chains of copper cations associated through a combination of offset-face-to-face (OFF) and edge-to-face (EF) π - π interactions, which run in the *a*-direction, separated by layers of water/methanol molecules and chloride anions held together by a network of hydrogen bonds (Fig. 4). The copper cations are also associated with water, methanol and chloride through

C18

Fig. 3. ORTEP diagrams of the molecular units of (a) $[Cu^{(1)}(dmp)_2]Cl \cdot MeOH \cdot 5H_2O$ (**2**), (b) molecular unit of the $[Cu^{(1)}(dmp) \cdot (H_2O)_2 \cdot C_6H_5PO_2(OH)] \cdot [C_6H_5PO_2(OH)] \cdot [C_6H_5PO_2$



C



Table 2

Significant bond angles (°) for compounds (1)-(6)

	(1) [4]	[Cu(phen) ₂]I [25]	(2)	(3)	(4)	(5)	(6)
N1-Cu-N2	80.85	82.27	82.90	79.69	82.61	88.05	88.35
N3-Cu-N4			82.67		82.84		87.63
N(2)-Cu-N(3)	95.14	106.82	116.58		130.00	91.95	92.35
N(1)-Cu-N(4)			117.10		107.48		91.94
N [*] -Cu-O (dpk)						74.16-75.30	73.67-75.03
N–Cu–O (H_2O)				102.07			
0-Cu-O (H ₂ O)				85.80			
0-Cu-O3 (phos-)				87.51			
Cu-03-P1				144.44			
Cl-Cu-N1	93.07						
Cl-Cu-N2	130.35						
Angle between amine planes	81.86	43.30	73.47		76.18	66.02	85.65

weak H-bonds (3.629–3.790 Å) between the methyl groups (C14–H14A \cdots O3, C27–H27A \cdots Cl', C28–H28A \cdots O6), and between the heterocyclic carbons of *dmp* (C28–H28B \cdots C1, C9–H9 \cdots O2, C2–

H2...Cl, C5–H5...Cl', C19–H19...Cl, C20–H20...O3, C16–H16...O5). The OFF interactions between the N1N2 *dmp* rings and those between the N3N4 *dmp* rings are perfectly parallel

Table 3				
Significant bond lengths	(Å) for compounds ((1)	-(6)

	(1) [4]	[Cu(phen) ₂]I [25]	(2)	(3)	(4)	(5)	(6)
Cu–Cl	2.647						
Cu–N1	1.989	2.008	2.02	1.993	2.032	2.001	2.007
Cu–N2	2.133		2.032	2.220	2.033	2.013	2.012
Cu–N3			2.033		1.997		2.008
Cu–N4			2.006		2.080		2.020
Cu–O (H ₂ O)				1.948-2.011			
Cu–O				1.965		2.459	2.418-2.425
P1-02	1.522			1.505	1.488		1.503
P1-01	1.501			1.513	1.525		1.512
P1-03	1.564			1.571	1.564		1.570
P2-04/04′				1.505	1.521/1.665		1.507
P2-05				1.510	1.538		1.516
P2-06				1.574	1.506		1.568



Fig. 4. Packing of (2) along a-axis showing EF/OFF stacked copper 'ribbons' separated by layers of H-bonded water and chloride layers.

with interplanar distances of 3.388 Å and 3.387 Å, respectively, and the EF interaction between the N1N2 *dmp* ligand framework and the methyl protons of the N3N4 *dmp* ligand (H28B') occurs at a distance of 2.716 Å (H28B' to plane C1 ring). All π - π interactions observed in (**2**) are within recognised and reported limits [24].

The *phen* analogue of (2) is too unstable to isolate and is readily oxidised. Reaction with phenylphosphonic acid '*in situ*' yields blue crystals of $[Cu^{(II)}Cl(phen)_2][C_6H_5PO_2(OH) \cdot C_6H_5PO(OH)_2]$ (1). The structure of (1) was previously solved by Clarke et al. [4], and found to contain a molecular unit with a **5** co-ordinate $[Cu-(phen)_2Cl]^+$ cation, counter-balanced by a phenylphosphonic 'dimer' anion. This 'symmetrical' complex is assembled into 'ribbons' via a continuous OFF interaction between the outer surfaces of the phen rings: a common motif for phenanthroline complexes [24]. The acid dimer consists of a hydroxyl proton (H2a) shared equally (centrosymmetric) between the O2 and O2' atoms, resulting in an ionic,

strong, perfectly linear hydrogen-bond $(d(0 \cdots H) = 1.21(7) \text{ Å})$, O2– H2a–O2′ = 180.00°), with H2a lying on a centre of inversion. Adjacent acid dimers are connected through pairs of regular strength H-bonds $(d(H3a\cdots O1) = 1.784 \text{ Å}, O3-H3a-O1 = 169.22°)$. The alternation of these motifs forms H-bonded acid 'chains', which further associate via EF interactions of the phenyl rings (E = H14, H15), to form acid 'sheets'.

The reaction of $[Cu^{(1)}(dmp)_2]Cl \cdot MeOH \cdot 5H_2O(2)$ with phenylphosphonic acid, via the '*stepwise*' route, resulted in a green crystalline product $[Cu^{(11)}(dmp) \cdot (H_2O)_2 \cdot C_6H_5PO_2(OH)]^+$ $[C_6H_5PO_2(OH)]^-(3)$. Single crystal analysis revealed a Cu(II) species with 5-coordinate, distorted trigonal-bipyramidal geometry. The bidentate *dmp* ligand and one water molecule occupy equatorial positions, whilst the other water molecule and a phenylphosphonate ligand occupy the distorted axial positions (Fig. 3b and Tables 2 and 3) i.e. a composition and structure rather different to the *phen* analogue (1) [4]. Strong intramolecular interactions are pres-



Fig. 5. The motifs observed in (3) (a) colour coding of molecular unit, (b) the H-bonded 'ladders' and (c) connection of the 'ladders' to form extended polymeric layers.

ent: hydrogen bonding occurs between the bound water molecules of the cation and the O6 and O8 oxygen atoms of the counter-balancing phenylphosphonate anion (O1–H1A···O8–2.683 Å, 161.7(1)°; O2–H2B···O6–2.722Å, 170.1(2)°), forming an R2,2(8) motif (Fig. 5); and OFF π – π interactions between the bound acid anion and the *dmp* ring (3.342 Å, 173.3(4)°).

The molecular unit interacts with its inverted neighbour by forming an R2,4(8) H-bonding motif between alternate water ligands and oxygen atoms of the free acid anion. An R2,2(10) motif linking the free acid anion through O7–H7A to O4' of an adjacent bound acid and a neighbouring bound water molecule (O2) to

the same free acid anion through O8 is also present. These individual H-bonding interactions combine to produce H-bonding '*ladders*' which run along the *b*-direction of the crystal. A symmetrical H-bonding pair also forms between O4…H5A'-H5/, and O5-H5A…O4' of adjacent bound acid anions (2.612 Å, 169.8(2)°) (Fig. 5c), which connect the '*ladders*' together to form extended polymeric layers.

Association between layers is achieved through OFF interactions between neighbouring *dmp* ligands (3.275 Å, 180°), and EF interactions between bound and free acids at an angle of $24.1(8)^{\circ}$ to the normal and a distance of 3.988 Å between C25' and the cen-



Fig. 6. The alternate stacking of the diagonally packed 'stepwise' $[Cu(dmp) \cdot (H_2O_2 \cdot C_6H_5PO_2(OH)]^* [C_6H_5PO_2(OH)]$ (3) viewed along the *c*-axis.



Fig. 7. The strong H-bonding interactions that occur between disordered acids and acid anions in (4).

troid of C16–21, which are typically found with $M(phen)_n$ crystal structures [11]. The 5-coordinate Cu(II) metal ion alternates with the phenylphosphonate counter-anion and a diagonal-type stacking is observed (Fig. 6).

In the case of the '*in situ*' compound (**4**), further structural analysis confirmed that it contained a 4-coordinate, distorted tetrahedral $[Cu^{(1)}(dmp)_2]^+$ cation (Tables 2 and 3 list selected bond lengths and angles), created by the coordination of a Cu(I) ion to the two nitrogen atoms of two bidentate *dmp* ligands (Fig. 3c), and that the phenylphosphonate dimer anion of (**1**) [4] had been replaced

by a disordered acid molecule (occupancies of O4 and O4' 0.632 and 0.368, respectively), and a phenylphosphonate anion, giving a molecular unit of formula $[Cu^{(1)}(dmp)_2]^+ \cdot [C_6H_5PO_3H_2]_{C_6}$ $C_6H_5PO_3H]^-$ (**4**). A very strong H-bond exists between the disordered acid and acid anion which is almost linear (175.13°) and has a length of 2.228 Å (centroid O4/O4'-H4A-O2) (Fig. 7), as compared to 180° and 2.439 Å, respectively, for the O2–H2A–O2 dimer linkage in (**1**) [4]. There is also an intramolecular EF interaction between the protons of the disordered acid and the aromatic ring of the anion (H40-plane C29–C34 2.845 Å, angle between planes



Fig. 8. local interactions in (4) (a) the OFF interactions between dmp aromatic rings, (b) the EF interactions between the dmp methyl protons and the dmp ring system.



Fig. 9. The H-bonded phosphonic acid/phosphonate chains which run through the structure and interact with the $[Cu(dmp)_2]^*$ cations through EF π - π stacking.

C29–C34 and C35–C40 = 75.99°), and between the methyl groups and the aromatic *dmp* rings (Fig. 8).

The packing of (**4**) has similarities to (**1**) [**4**] in that the acids/anions form extended H-bonded chains, and OFF interactions exist between the *dmp* ligands, but the latter are isolated, not extended, ribbon-like structures, and the chains of acids are not connected directly to each other through EF interactions. Thus the substituted methyl groups of *dmp* do not prevent intercalation of the complexed copper(I) cation between the self-assembled phenylphosphonate dimers, but they do disrupt the extended packing motifs. In (**4**), the acid chains form via the aforementioned EF interaction and via two separate H-bonding interactions: an R2,2(8) motif connecting the disordered acids within each molecular unit (O5–H5A–O6:2.500 Å, 167.83°), and an R2,2(8) motif connecting the acid anions (O1–H1A–O3: 2.533 Å, 167.83°) (Figs. 7 and 8).

The $[Cu^{(1)}(dmp)_2]^+$ cations are connected through two separate, perfectly parallel OFF interactions between the N1N2 rings and between the N3N4 *dmp* rings (N1N2:3.465 Å; N3N4:3.549 Å), and an OFF interaction also exists between the N3N4 *dmp* rings and the disordered acid (N3N4 plane: centroid C35–C40:3.553 Å, 163.26°) (Figs. 8 and 9).

3.6.2. Structures of compounds (5-6) – di-2-pyridylketone derivatives

Single crystal X-ray diffraction of (**5**) confirmed the +2 state of copper and revealed an asymmetric unit having a Cu(II) centre bound to a tridentate N,N,O chelating *dpk* ligand that has undergone hydrolysis at the carbonyl group (*dpk* · H₂O) (Fig. 10). Also present were two water molecules and a charge-balancing chloride anion. Therefore, the molecular unit contains a 6-coordinate (octahedral) Cu(II) ion coordinated to two *dpk* · H₂O ligands, charge-balanced by two chloride ions. Four water molecules intercalate within the lattice and add to the overall packing in the $[Cu^{(II)}(dpk \cdot H_2O)_2]Cl_2 \cdot 4H_2O$ (**5**) crystal. Thus, the composition and structure are identical to that of a material previously published by Wang et al. [17], however the unit-cell dimensions are marginally smaller, and the R factor is improved.

A stronger interaction is observed between the Cu(II) and N than between Cu(II) and O, as indicated by the substantially short-



Fig. 10. (a) asymmetric unit of the blue/purple intermediate (5) and (b) the three planes that pass through the copper centre of $[Cu(dpk \cdot H_2O)_2] Cl_2 \cdot 4H_2O$.



Fig. 11. H-bonding motifs observed between water and chloride ions in (5).



Fig. 12. Hydrogen bonded ribbons of $[Cu^{(II)}(dpk \cdot H_2O)_2] Cl_2 \cdot 4H_2O$ (5) viewed along *b*-axis, with R4,2(12) motif.

er bond lengths in the former (Cu–N1 = 2.001 Å, Cu–O1 = 2.458 Å) (Tables 2 and 3). These results concur with those of Serna et al. [14] and Wang et al. [17] who witnessed similar structural arrangements in other $[M(dpk \cdot H_2O)_2]^{2+}$ cations.

Hydrogen bonding is responsible for the predominant interaction between the cations in the structure. These occur between O4–H4A of a hydrated oxygen and O1 of a water molecule (2.727 Å) which, in turn, forms another H-bond with another hydrated oxygen (O3'–H3A') (2.733 Å) in an adjacent molecule resulting in a repeating R4,2(12) motif and a H-bonded ribbon of $[Cu^{II}(dpk \cdot H_2O)_2]Cl_2 \cdot 4H_2O$ cations and water molecules along the *b*-axis (Fig. 11). These ribbons interact via further H-bonding between water molecules (O2) (2.658 Å) and chloride anions to produce linked R6,4(12) and R2,4(8) motifs (Fig. 12), and through OFF interactions between aromatic π -electrons in the pyridyl rings (2.676 Å) of the cations in each layer (Fig. 13). Single crystal analysis of (**6**) revealed the same 6-coordinate Cu(II) cation as observed in the intermediate (**5**) (Fig. 3d). However, the perfect symmetry of the $[Cu^{II}(dpk \cdot H_2O)_2]^+$ cation was not retained (Tables 2 and 3). The chloride counter ions in the intermediate product have been displaced by two phenylphosphonate anions, together with a highly disordered phenylphosphonic acid. The disordered acid appears to have an equivalent void volume of a fully-protonated phenylphosphonic acid and is intercalated within the crystal structure, filling vacancies within the lattice and engaging in complex hydrogen-bonding with the free phosphonate anions.

Packing diagrams show non-linear H-bond links occurring between oxygen atoms, attributed to the hydrated dpk ligands interacting with the phenylphosphonate dimers forming the skeletal sheets of the packing structure (Fig. 14). H-bonding interactions also occur between O8 and O7 of the acid molecules, which



Fig. 13. π - π interactions between parallel pyridine rings viewed along the *b*-axis in (5).



Fig. 14. Non-linear alternating H-bonding between the phenylphosphonate dimers, as well as linking towards the disordered acid layer in (**6**).

support the interleaved, disordered acid molecules, and build the layers of the structure. Figs. 15 and 16 clearly show the disordered acid interleaved between the sheets of the alternating cations and phenylphosphonates. Adding to stability of the structural packing are columns formed by OFF and EF π – π interactions between the phenyl rings. Notably, OFF contacts occur from *dpk* pyridine rings aligned to a phenylphosphonate anion at a distance of 4.343 Å. OFF interactions and EF interactions also occur from the edge of the same phenylphosphonate molecule to the opposite *dpk* pyridine ring on the octahedral [Cu^{II}(dpk · H₂O)₂ · 2Cl⁻ · 4H₂O] cations (Fig. 17).

4. Conclusions

It was found that the use of 2,9-dimethyl-1-10-phenanthroline (dmp) instead of unsubstituted phenanthroline (phen) produced a stable, readily isolable 4-coordinate Cu(I) product (**2**), i.e., the increased steric hindrance in the 'bite' area of dmp did not prevent coordination with the metal but it did provide protection against

oxidation, which was not observed during the preparation of the copper–*phen* analogues [4].

The addition of phenylphosphonic acid produced two structures from alternative synthetic routes. An 'in situ' process yielded red block Cu(I) crystals, with dimeric phenylphosphonate counter anions (4) replacing the chloride ion of (2). However, if the intermediate (2) was isolated from solution prior to addition of the acid ('stepwise' process) a green, needle-like Cu(II) complex formed, whereby a *dmp* ligand was replaced by a phenylphosphonate ion (3) and two water molecules. It was concluded that the balance between steric pressures and bond strength around the metal centre was delicate, and that addition of an extra mole of the *dmp* ligand to the 'stepwise' intermediate (2), before the addition of the phenylphosphonic acid (ligand addition process) may force the ligand- $[Cu(dmp)_2]^+$ coordination eauilibrium towards the $[C_6H_5PO_3H_2 \cdot C_6H_5PO_3H]^-$ product (4). This hypothesis proved correct, and also resulted in an ideal synthetic route to (4) which was isolated in maximum yield (99%). Thus, even in the presence of acidic oxidising conditions the bulky methyl substituents of dmp were able to protect the metal centre, and provide redox control.

The structure and composition of (**4**) was subtly different to the phenanthroline analogue, $[Cu^{(II)}Cl(phen)_2]^+ \cdot [C_6H_5PO_3H_2 \cdot C_6H_5PO_3H]^-$ (**1**) [**4**], since, the slightly bulky methyl-substituents of the *dmp* had some influence on global packing. Indeed the OFF π - π stacked ribbons of copper complexes in (**1**) were replaced by alternating pairs of OFF and EF stacked complexes in (**4**), and the layers of H-bonded acids were replaced by isolated chains. The structure of product (**3**) was very different to both (**1**) and (**4**) owing to the cleavage of an amine ligand and its replacement by water and a coordinated acid anion. The latter enabled the formation of a polymeric layered material where the copper cations were connected to the free acid anions via a series of intra- and intermolecular H-bonds.

The luminescent activity reported for copper(I) *dmp* salts [11–14] was also observed in (**2**), with a strong emission band at \sim 730 nm following excitation at 400 nm. This activity was retained and slightly enhanced, when the *dmp* complex was incorporated into a phosphonate network (**4**), and is ascribed to the extended pi system present in the phosphonate supramolecular assembly.

Like the unsubstituted *phen* and *bipy* ligands, the sterically open dpk ligand did not prevent oxidation of the Cu(I) metal centre, and a purple/blue 6-coordinate bis dpk Cu(II) species was formed, $[Cu^{(II)}(dpk \cdot H_2O)_2]$ $Cl_2 \cdot 4H_2O$ (5), in which the dpk ligand underwent hydration to produce the gem-diol [15], capable of coordinating with the copper ion through tridentate N,N,O bonding. Thus, a 6-coordinate copper(II) cation, exhibiting the well-known Jahn-Teller tetragonal distortion typical of Cu(II) complexes is observed, in contrast to the 5-coordinate species in (1) [4], and the presence of the two OH groups in the cation of (6/6a) provides it with improved H-bonding potential. The latter resulted in the formation of a polymeric chain of copper cations linked by the OH groups of the diol and the intercalated water molecules. Reaction of (5) with phenylphosphonic acid by both the ligand addition and in situ routes produced similar products (6 and 6a). The 6-coordinate geometry and composition of the cationic Cu(II) species was retained, whilst the Cl- counter ions were replaced by two phenylphosphonate anions and a highly-disordered, fully-protonated phenylphosphonic acid: $[Cu^{(II)}(dpk \cdot H_2O)_2] \cdot [C_6H_5PO_2(OH)]_2 \cdot$ $[C_6H_5PO(OH)_2]$ (6 and 6a). The familiar H-bonding R2,2(8) motifs were again present, this time forming between the acid anions, and also between bound OH groups and acid anions. The disordered acid being intercalated between the layers of H-bonded and $\pi - \pi$ stacked cations and anions.

Clearly, the comparative studies described here using *phen*, *bipy*, *dpk* and the substituted *phen* derivative (*dmp*), provide good evidence for the delicate balance between steric crowding, coordi-



Fig. 15. Sheets of alternating H-bonding phenylphosphonate dimers and the cation in (6), with the disordered acid occupying the voids between the sheets. Viewed along the *b*-axis.



Fig. 16. Packing of the 'step wise' product viewed along along the *c*-axis.



Fig. 17. The OFF and EF interactions forming aromatic columns in (6): a = 4.343, b = 4.190, c = 2.674 Å

nation number, bond strength and oxidation state in these copper(I/II) complexes, and it is the overall interaction of all of these factors which determines the final structure adopted by the supramolecular array.

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Appendix A. Supplementary material

CCDC 692110, 692112, 692113 and 692114 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.09.010.

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