



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(I) species, $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{Cl} \cdot \text{MeOH} \cdot 5\text{H}_2\text{O}$ (**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, CrystEngComm. 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, $[\text{Cu}^{\text{I}}(\text{dmp})_2] \cdot [\text{C}_6\text{H}_5\text{PO}_3\text{H}_2 \cdot \text{C}_6\text{H}_5\text{PO}_3\text{H}]$ (**4**), whilst recrystallisation of (**2**) prior to addition of the acid ('stepwise' process) produced a green, needle-like Cu(II) complex, $[\text{Cu}^{\text{II}}(\text{dmp}) \cdot (\text{H}_2\text{O})_2 \cdot \text{C}_6\text{H}_5\text{PO}_2(\text{OH})] [\text{C}_6\text{H}_5\text{PO}_2(\text{OH})]$ (**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, $[\text{Cu}^{\text{I}}\text{Cl}(\text{phen})_2] \cdot [\text{C}_6\text{H}_5\text{PO}_2(\text{OH}) \cdot \text{C}_6\text{H}_5\text{PO}(\text{OH})_2]$ (**1**) [R. Clarke, K. Latham, C. Rix, M. Hobday, J. White, CrystEngComm. 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, $[\text{Cu}^{\text{II}}(\text{dpk} \cdot \text{H}_2\text{O})_2] \text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (**5**), and $[\text{Cu}^{\text{II}}(\text{dpk} \cdot \text{H}_2\text{O})_2] \cdot [\text{C}_6\text{H}_5\text{PO}_2(\text{OH})_2 \cdot \text{C}_6\text{H}_5\text{PO}(\text{OH})_2]$ (**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 $(\text{R}-\text{P}(\text{O})(\text{OH})_2)$. Like sulphonic acids, phosphonic acids are strong acids, with the first $\text{pK}_a \approx 1-2$, 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 $[\text{C}_6\text{H}_5\text{PO}(\text{OH})_2]$ [3–5], and those acids that have multiple functionalities and may form zwitterions, e.g., *N*-nitritotri(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: $[\text{Cu}^{\text{II}}(\text{phen})_2\text{X}][(\text{O}-\text{H})_2\text{OPC}_6\text{H}_5][(\text{OH})\text{O}_2\text{PC}_6\text{H}_5]$ (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 $\pi-\pi$ 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 $[\text{Cu}^{\text{II}}(\text{phen})_2\text{Cl}][(\text{OH})_2\text{OPC}_6\text{H}_5]$ ($(\text{OH})_2\text{O}_2\text{P}_6\text{H}_5$) (**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 $[\text{Cu}^{\text{I}}(\text{phen})_2\text{X}]$ (X = Cl⁻, Br⁻) spontaneous oxidation to Cu(II), to produce $[\text{Cu}^{\text{II}}(\text{phen})_2\text{Cl}][(\text{OH})_2\text{OPC}_6\text{H}_5]$ ($(\text{OH})_2\text{O}_2\text{P}_6\text{H}_5$) (**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 $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$ 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 Kα radiation (λ = 1.5406 Å): scan range 3–60° 2θ, 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. $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{Cl} \cdot \text{MeOH} \cdot 5\text{H}_2\text{O}$ (**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 dark-red 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 $[\text{C}_{28}\text{H}_{24}\text{N}_4\text{CuCl}]$: 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%.

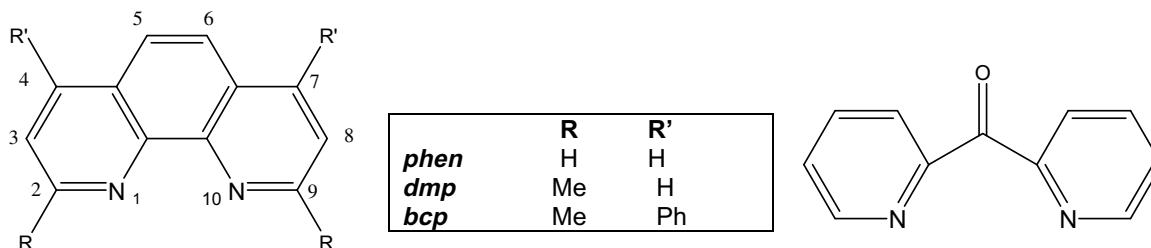


Fig. 1. (a) 1,10-Phenanthroline and its derivatives and (b) di-2-pyridyl ketone (*dpk*).

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