Synthesis and structures of copper(II) anion-bridged aggregates and chains: control over molecular shape ‡

Anne C. Deveson,[a] Sarah L. Heath,[a] Charles J. Harding[b] and Annie K. Powell *,†,[a]

[a] *School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, UK*
[b] *Department of Chemistry, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK*

Di-2-pyridyl ketone (dpk) can complex metal ions in its activated $[(NC_5H_4)_2C(OR)(OH)]$ or non-activated form. In its activated form it displays a dinucleating behaviour as manifested by the compounds $[\{Cu_2[(NC_5H_4)_2C(OEt)O]Cl_3(EtOH)\}_2]$ and $[\{Cu_2[(NC_5H_4)_2C(OMe)O]Cl_3\}_\infty]$ (which also possess halide bridges). These compounds have been structurally characterised using single-crystal X-ray diffraction. In its non-activated form it acts as a simple bidentate chelate. The X-ray analysis of $[\{Cu(dpk)(NO_3)_2\}_\infty]$ revealed an anion-bridged structure where bridging nitrato groups link the copper centres. The π-stacking arrangements of these compounds are also considered.

Aggregation of clusters of metal atoms can provide molecular-based systems displaying properties which may find applications in molecular electronics or optical switching devices. Such clusters can be directly M–M bonded or consist of anion-bridged metal ions with these bridges transmitting electronic information to the metal ions to a greater or lesser degree. One of the major challenges for synthetic chemists is to understand how control over cluster shape, size and property can be achieved. It is only by synthesizing numerous examples of such compounds and monitoring their electronic properties that we can obtain the information necessary to enable us to produce materials displaying specific properties. As part of our exploration of ways to link together metal centres[1] we have chosen to study a system which favours one-dimensional chain structures and also produces crystal-packing effects *via* π–π interactions. Owing to Jahn–Teller distortion the copper co-ordination sphere is very flexible. It allows for longer semi-co-ordinate Cu–X bonds as well as normal Cu–X bonds where X is an anionic ligand,[2] hence asymmetric as well as symmetric bridges can be formed. These bridges may involve a finite number of copper(II) atoms or they may form an infinite polymeric species.[2] Most copper chains reported have been co-ordinated solely by halide ions. There are examples in the literature of chains of four-, five- and six-co-ordinate copper.[2–4]

Our objective was to synthesize materials which might exhibit both superexchange and π pathways for the transfer of electronic information. We describe here the synthesis and crystal structures along with preliminary magnetic investigations on three copper(II) systems and report two ways of creating one-dimensional chain molecules using di-2-pyridyl ketone (dpk) and anionic bridging moieties. One-dimensional chains are recognised to provide the simplest means of understanding molecular interactions in infinite systems. These concepts are discussed further in the review by Willett.[5] The dpk molecule offers the possibility of creating π–π interactions within a crystal structure. The presence of a divalent metal ion in solutions containing the molecule dpk can lead to activation of the keto-group resulting in the formation of diols or hemiketals in aqueous and alcoholic systems respectively.[6–8]
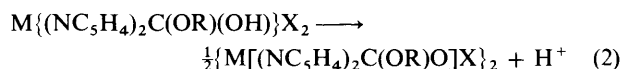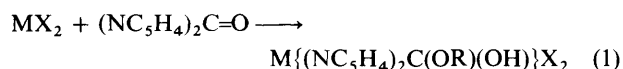
In alcoholic media we have found that for metal:ligand ratios of 1 : 1 an equilibrium process operates, equations (1) and (2). The reaction of ROH with a carbonyl moiety results in the
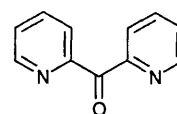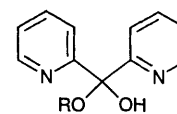
central carbon adopting a tetrahedral rather than trigonal stereochemistry. This has the effect of angling the pyridyl rings resulting in novel π-stacking arrangements in the crystal lattices. When X = halide the monomeric $M\{(NC_5H_4)_2C(OR)OH\}X_2$ form predominates *e.g.* for M = Zn, R = Et and X = Br and Cl and for M = Cu, R = Me **1** or Et **2** and X = Cl. The structure for M = Cu, R = Me and X = Cl is shown in Fig. 1. In these systems for both copper and zinc the OR group points towards the metal and is within bonding distance for M = Cu. However for X = NO_3^- the dinuclear $\{M[(NC_5H_4)_2C(OR)O]X\}_2$ forms preferentially.[7] Fig. 2 shows the structure for M = Zn, R = Me and X = NO_3^-; see structure of **3** (M = Cu) is believed to be analogous (see below). In these systems the hemiketal form of the ligand bridges the metal centres through the deprotonated hydroxy group and the OR group points away from the metal. This bridging mode was also observed in the previously reported dinuclear copper complex $[Cu_2\{(NC_5H_4)_2C(OEt)O\}(pz)Cl_2]$ where each copper has a bridging hemiketal ligand and a bridging pyrazolate (pz) with chloride ions taking the remaining co-ordination sites.[8] This dinucleating behaviour can be exploited to produce larger aggregates by linking together dinuclear units using halide bridges as we describe here. We also report how nitrate anions can link mononuclear units formed from Cu^{2+} and the non-activated form of the ligand.

dpk

R = H, Me or Et

$$MX_2 + (NC_5H_4)_2C{=}O \longrightarrow$$
$$M\{(NC_5H_4)_2C(OR)(OH)\}X_2 \quad (1)$$

$$M\{(NC_5H_4)_2C(OR)(OH)\}X_2 \longrightarrow$$
$$\tfrac{1}{2}\{M[(NC_5H_4)_2C(OR)O]X\}_2 + H^+ \quad (2)$$
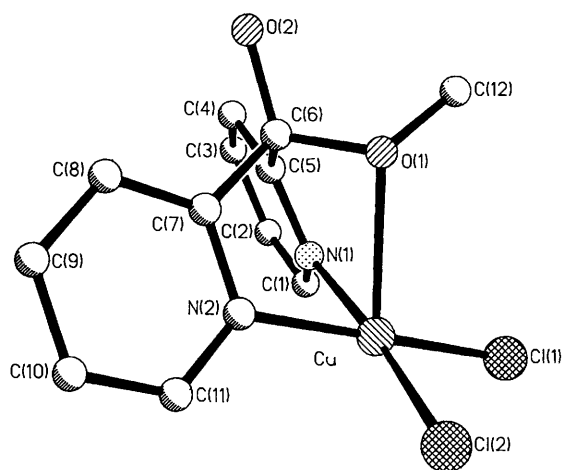
Fig. 1 Molecular structure of [Cu{(NC$_5$H$_4$)$_2$C(OMe)(OH)}Cl$_2$]
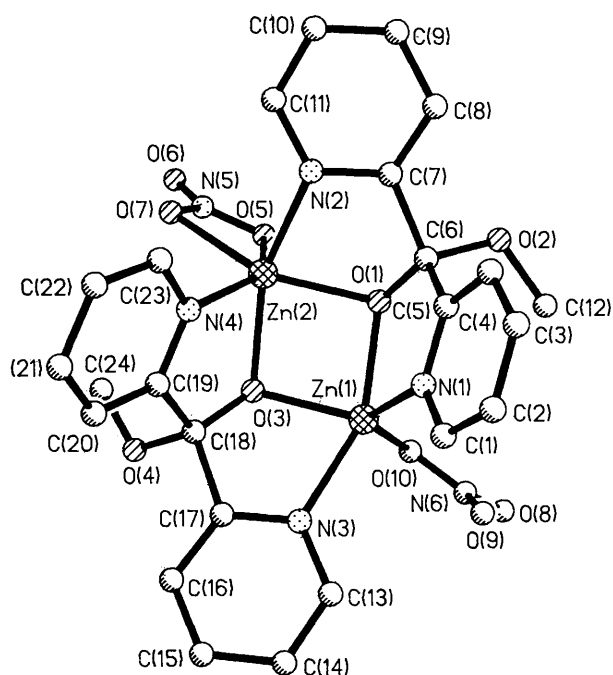
Fig. 2 Molecular structure of [Zn$_2${(NC$_5$H$_4$)$_2$C(OMe)O}$_2$(NO$_3$)$_2$]

Experimental

All chemicals were used as received from Aldrich Chemical Company. Infrared spectra were recorded as KBr discs on a Mattson Galaxy spectrometer from 4000 to 400 cm^{-1} at 4 cm^{-1} resolution. Magnetic measurements were made on compounds **4** and **5** from room temperature to 4 K on an Oxford Instruments Electromagnetic Faraday susceptibility system A using a Hall probe to control the field.

Syntheses

The syntheses of compounds 1–3 were as described in ref. 7.

[{Cu$_2$[(NC$_5$H$_4$)$_2$C(OEt)O]Cl$_3$(EtOH)}$_2$] 4. A solution of dpk (0.12 g, 0.63 mmol) in ethanol (10 cm^3) was added to a solution of CuCl$_2$ (0.16 g, 1.25 mmol) in ethanol (10 cm^3) and stirred to form a clear dark green solution. After 1 d green crystals of complex **4** had formed and were filtered off. Yield 0.284 g, 44.4% (Found: C, 35.3; H, 3.6; Cl, 20.8; Cu, 25.6; N, 5.8. C$_{30}$H$_{38}$Cl$_6$Cu$_4$N$_4$O$_6$ requires C, 35.5; H, 3.7; Cl, 21.0; Cu, 25.0; N, 5.5%). The compound can also be synthesized using **2** as a precursor.

[{Cu$_2$[(NC$_5$H$_4$)$_2$C(OMe)O]Cl$_3$}$_\infty$] 5. A solution of dpk (0.12 g, 0.63 mmol) in methanol (10 cm^3) was added to a solution of CuCl$_2$ (0.16 g, 1.25 mmol) in methanol (10 cm^3) and stirred to form a clear dark green solution. After 1 d green crystals of complex **5** had formed and were filtered off. Yield 0.185 g, 65.4% (Found: C, 32.1; H, 2.4; Cl, 23.6; Cu, 27.8; N, 6.1. C$_{12}$H$_{11}$Cl$_3$Cu$_2$N$_2$O$_2$ requires C, 32.1; H, 2.45; Cl, 23.7; Cu, 28.3; N, 6.25%). The compound can also be synthesized using **1** as a precursor.

[{Cu(dpk)(NO$_3$)$_2$}$_x$] 6. A solution of dpk (0.103 g, 0.56 mmol) in acetonitrile (5 cm^3) was added to a solution of Cu(NO$_3$)$_2$·3H$_2$O (0.135 g, 56 mmol) in acetonitrile (5 cm^3) and stirred to form a clear dark blue solution. After 1 h blue crystals of complex **6** had formed and were filtered off. Yield 0.016 g, 8% (Found: C, 36.1; H, 2.1; Cu, 16.1; N, 15.0. C$_{11}$H$_8$CuN$_4$O$_7$ requires C, 35.5; H, 2.2; Cu, 17.1; N, 15.1%).

Crystallography

Compound 4. *Crystal data.* C$_{15}$H$_{19}$Cl$_3$Cu$_2$N$_2$O$_3$, $M =$ 508.7, monoclinic, space group $P2_1/n$, $a =$ 8.334(2), $b =$ 14.758(4), $c =$ 16.132(4) Å, $\beta =$ 90.19(2)°, $U =$ 1984.1(9) Å^3, $Z = 4$, $D_c = 1.703$ g cm^{-3}, $F(000) = 1024$, $\mu = 2.576$ mm^{-1} for Mo-Kα radiation ($\lambda = 0.710\,73$ Å), crystal size 0.18 × 0.23 × 0.30 mm.

Data collection and reduction. Data were collected on a Siemens R3m/V diffractometer. Index range h −9 to 0, k 0–17, l −19 to 19. No significant intensity variation was observed for two standard reflections measured every 50. 3935 Reflections were collected of which 3508 were independent and 2314 considered observed [$F > 4\sigma(F)$]. No correction for absorption was applied.

Structure solution and refinement. The structure was solved by location of heavy atoms using a Patterson map and refined by a full-matrix least-squares approach using the SHELXTL PLUS[9] software package. All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. Hydrogen atoms on the ligand were located after successive cycles of least-squares refinement on F and constrained to idealised positions. Parameters refined = 229, $R = 0.0628$, $R' = 0.0915\%$, where R and R' are defined as $\Sigma|F_{obs} - F_{calc}|/\Sigma F_{obs}$ and $(\Sigma w|F_{obs} - F_{calc}|^2/\Sigma wF_{obs}^2)^{\frac{1}{2}}$, with a weighting parameter in $w^{-1} = \sigma^2(F) + gF^2$, $g = 0.005$, goodness of fit $S = 1.09$, maximum shift/e.s.d. = 0.024, no features in the final difference map outside the range −1.24 to 1.07 e Å^{-3}. Data to parameter ratio 10.1:1. Selected bond lengths and angles are given in Table 1.

Compound 5. *Crystal data.* C$_{12}$H$_{11}$Cl$_3$Cu$_2$N$_2$O$_2$, $M = 448.7$, triclinic, space group $P\bar{1}$, $a = 7.761(2)$, $b = 8.867(2)$, $c = 11.921(2)$ Å, $\alpha = 78.35(3)$, $\beta = 76.43(3)$, $\gamma = 66.70(3)°$, $U = 726.4(3)$ Å^3, $Z = 2$, $D_c = 2.051$ g cm^{-3}, $F(000) = 444$, $\mu = 3.497$ mm^{-1} for Mo-Kα radiation, crystal size 0.16 × 0.16 × 0.20 mm.

Data collection and reduction. Data were collected on a Stoe IPDS system. Index range h −10 to 10, k −11 to 11, l −14 to 14. 11 448 Reflections were collected of which 3105 were independent and 2797 considered observed [$F > 6\sigma(F)$]. No correction for absorption was applied.

Structure solution and refinement. The structure was solved and refined on F as for compound **4**. Parameters refined = 190, $R = 0.073$, $R' = 0.1087$, with $g = 0.008$, $S = 1.13$, maximum shift/e.s.d. = 0.11, no features in the final difference map outside the range −1.87 to 1.01 e Å^{-3}. Data to parameter ratio 14.7:1. Selected bond lengths and angles are given in Table 2.

Compound 6. *Crystal data.* C$_{11}$H$_8$CuN$_4$O$_7$, $M = 371.75$, orthorhombic, space group $P2_12_12_1$, $a = 4.9116(10)$, $b = 14.448(9)$, $c = 19.131(4)$ Å, $U = 1357.6(9)$ Å^3, $Z = 4$, $D_c =$

1.819 g cm^{-3}, $F(000) = 748$, $\mu = 1.655$ mm^{-1} for Mo-Kα radiation, crystal size 0.20 × 0.10 × 0.15 mm.

Data collection and reduction. Data were collected on a Rigaku AFC7R diffractometer. Index range h −5 to 5, k 0–17, l −22 to 22. 4751 Reflections were collected of which 2387 were independent. No correction for absorption was applied.

Structure solution and refinement. The structure crystallises as a racemic twin and account was taken of this in the refinement. It was solved by location of heavy atoms using direct methods and SHELXTL PLUS[9] and refined by a full-matrix least-squares approach using SHELXL 93.[10] All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. Hydrogen atoms of the ligand were fixed in idealised positions with a riding model and a fixed isotropic U. Parameters refined = 209, R = 0.0481, based on F as before and $wR2$ = 0.0916, based on F^2, such that $wR2$ = $[\Sigma w|F_{obs}^2 - F_{calc}|^2/\Sigma w(F_{obs}^2)^2]^{\frac{1}{2}}$, with g = 0.0386, S = 1.018, maximum shift/e.s.d. = 0.000. No features in the final difference map outside the range −0.431 to −0.498 e Å^{-3}. Data to parameter ratio 11.42:1. A correction for secondary extinction was applied, ζ = 0.0017(7). Selected bond lengths and angles are given in Table 3.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/116.

Results and Discussion

Structures of compounds 1–6

The structures of compounds **1** and **2** have been described previously.[7] Both display a square-pyramidal co-ordination geometry around the copper (classically described as 4 + 1) with the halides and the nitrogen atoms of the ligand forming a basal plane and the oxygen of the OR group of the hemiketal in the apical site. From infrared analysis the structure of **3** appears to be analogous to that of the previously described zinc dimer[7] [Zn₂{(NC₅H₄)₂C(OMe)O}₂(NO₃)₂] (Fig. 2). This bridging mode of the modified dpk ligand is also observed in the basic building block of compounds **4** and **5** consisting of a dinuclear copper unit with the two copper atoms bridged by the deprotonated hydroxyl of the hemiketal from the modified dpk ligand and one chloride ion and further co-ordination to each copper atom from the pyridyl nitrogen atoms of the modified dpk ligand. In **4** a tetranuclear structure results with two such building blocks linked together by a dichloride bridge, Cl(2) and the symmetry equivalent Cl(2a) (Fig. 3) and the chain is terminated by one chloride ion and an ethanol molecule from the solvent. In **5** however there are no terminal solvent molecules and the dimeric units are linked together *via* dichloride bridges to form an infinite chain (Fig. 4). The two central copper centres, Cu(1) and Cu(1a) in both **4** and **5** linked by dichloride bridges are slightly closer for **4** than for **5** (3.46 and 3.63 Å apart, respectively) whilst the link within the building block is longer for **4** (3.01) than **5** (2.95 Å). For **6** the dpk ligand retains its carbonyl function, as a result of the synthesis being carried out in an ROH-free medium and this takes no part in metal binding. Thus the ligand is bidentate and three further co-ordination sites on the copper are taken by one monodentate and two bridging nitrate ligands, one of which is from a symmetry-related ligand resulting in the formation of an infinite structure. This latter bridging nitrato oxygen has the longest copper to ligand bond length at 2.339(6) Å, all other such distances lying in the range 1.943(5)–2.015(5) Å (Table 3). Fig. 5 shows the basic building block of the infinite structure.

The co-ordination geometry of the copper centres in all three compounds **4–6** is approximately trigonal bipyramidal, this
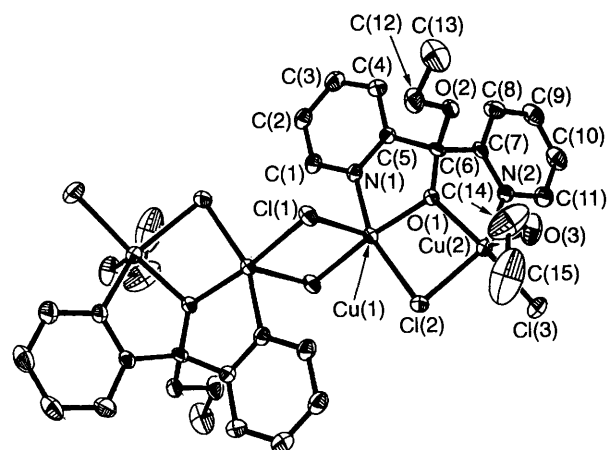

Fig. 3 Molecular structure of [{Cu₂[(NC₅H₄)₂C(OEt)O}Cl₃(EtO-H)}₂] **4**. Ellipsoids correspond to 30% probability
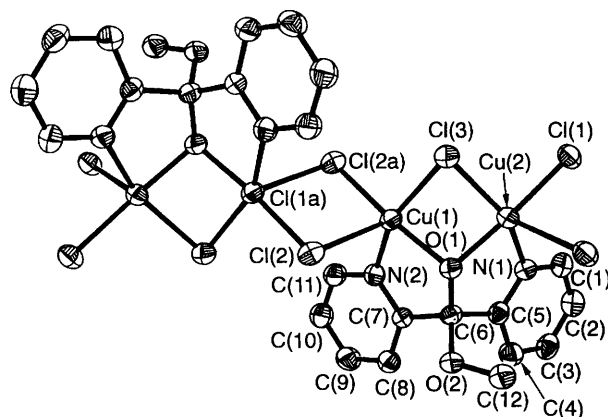
Fig. 4 Molecular structure of [{Cu₂[(NC₅H₄)₂C(OMe)O]Cl₃}∞] **5**. Ellipsoids correspond to 50% probability
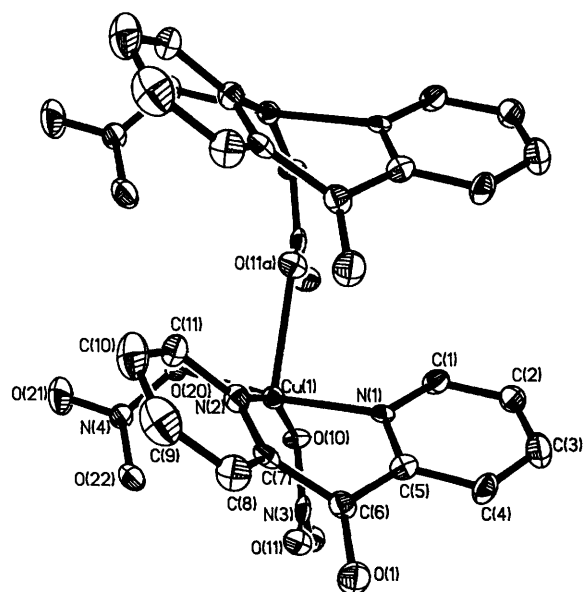
Fig. 5 The building block of [{Cu₂(dpk)(NO₃)₂}∞] **6**. Ellipsoids correspond to 30% probability

form of five-co-ordination offering an alternative route to relieving the degeneracy of unequally unoccupied d orbitals to either square-based pyramidal geometry (4 + 1), or, indeed, tetragonally distorted 4 + 2 geometry. The co-ordination of the central copper atoms for both **4** and **5** is completed by ligation from one pyridyl N, resulting in an overall CuCl₃ON environment with the geometry somewhat more regular for **5**

than 4. For 4 Cu(1) is 0.236 Å out of the equatorial plane defined by N(1), Cl(1) and Cl(2) whilst for 5 Cu(1) is 0.197 Å out of the plane defined by N(2), Cl(2) and Cl(3). The outer copper atoms are also five-co-ordinate, with the bridging chloride and OR from the ligand already mentioned, a pyridyl N, and for 4 a terminal chloride and one ethanol molecule completing the co-ordination sphere to give an overall $CuCl_2O_2N$ environment. For 5 the ethanol is replaced by a second chloride to give a $CuCl_3ON$ environment. In 4 Cu(2) is 0.243 Å out of the plane defined by N(2), Cl(2) and O(3) and in 5 Cu(2) is 0.184 Å out of the plane defined by N(1), Cl(1a) and Cl(3). In 6 the trigonal plane is formed by N(1), O(20) and the symmetry equivalent O(11a) with the copper only 0.073 Å out of this plane; N(2) and O(10) occupy the apical sites.

It has been shown that magnetic properties of copper(II) aggregates can often be correlated with structural parameters.[2-5] These are of relevance to compounds 4 and 5. For any pair of bridged copper centres, $X_2Cu(\mu\text{-}L)_2CuX_2$, the parameters φ, the Cu–L–Cu angle, τ, the twist angle between the CuX_2 and Cu_2L_2 planes, and δ, the angle between the CuX_2L_2 planes, can be important in determining the extent of interaction between the two copper centres. For 4 the value of τ corresponds to the angle between the planes defined by Cu(1), Cu(2), O(1), Cl(2) and Cu(1), Cl(1) and Cl(1a) (where a refers to the inversion-related atoms) and is 72°. For 5 the corresponding planes defined by Cu(1), O(1), Cu(2), Cl(3) and Cu(1), Cl(2) and Cl(2a) are angled at 63° to each other. The δ angles subtended by the planes Cu(2), O(1), O(3), Cl(2), Cl(3) and Cu(1), O(1), Cl(2), Cl(1), Cl(1a) in 4 and Cu(2), Cl(1), Cl(1b), O(1), Cl(3) and Cu(1), O(1), Cl(3), Cl(2), Cl(2a) in 5 and are 17.6 and 7.0° respectively, whilst the δ angles between the $CuOCl_3$ planes are zero for both compounds. The φ bridging angles range from 81.5 to 89.5° for 4 and 78.7 to 93.7° for 5 (Tables 1 and 2).

The packing arrangements for all three compounds 4–6 are markedly different. In 4 the tetranuclear units link together in the lattice via hydrogen bonds from the terminal chloride and oxygen atoms of the terminal ethanol at 3.13 Å to form chains as shown in Fig. 6. Within these chains all the coppers are coplanar. These extended chains stack in the crystal lattice (Fig. 7) to optimise π interactions between the pyridyl rings (i.e. they eclipse one another) which are 8.33 Å apart. The pyridyl rings within the ligand are angled at 60.8° to each other producing a ripple of π-stacking interactions throughout the lattice. As noted above, a truly infinite structure could result if the ethanol were replaced by a Cl, which would then form a bridge with the other terminal Cl to a further copper centre in the pattern as is observed for Cu(1), Cu(1a), Cl(1), Cl(1a). The infinite structure thus produced would also be neutral. However, the packing

observed for the infinite structure isolated here, 5, is very different as a consequence of a new π-stacking arrangement where although the rings are nearer they are staggered along a zigzag line (Fig. 8). There are two distances observed between pairs of rings of 5.13 and 4.25 Å. The pyridyl rings within the ligand are angled at 72.1° to each other. Within the individual chains the coppers are not quite coplanar (average deviation 0.016 Å). In 6 there is another form of π-stacking arrangement. The lattice viewed down the b axis (Fig. 9) shows how an essentially one-dimensional zigzag structure results with all the coppers collinear and coplanar. The pyridyl rings of the ligand are angled at 39.4° to each other, a smaller angle than is observed for 4 or 5 as a consequence of the trigonal geometry being preserved at the carbonyl carbon. The rings stack in an eclipsed arrangement at a distance of 4.91 Å (constrained to be the same as the Cu · · · Cu distance). The pyridyl rings of one chain are angled at 68° to the rings of neighbouring chains with a closest approach of approximately 4.4 Å. When viewed down the a axis the stacking of these chains can be seen to result in the formation of channels running through the crystal structure (Fig. 10).
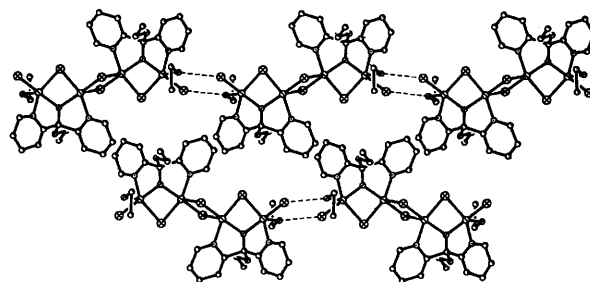

Fig. 6 Packing of complex 4 viewed down the a axis showing the linking of the tetramer units

Table 2 Selected bond lengths (Å) and angles (°) for [{Cu$_2$[(NC$_5$-H$_4$)$_2$C(OMe)O]Cl$_3$}$_\infty$] 5

Cu(1)–O(1)	1.977(3)	Cu(2)–O(1)	1.941(3)
Cu(1)–N(2)	1.982(5)	Cu(2)–N(1)	2.003(5)
Cu(1)–Cl(2)	2.717(1)	Cu(2)–Cl(1)	2.253(1)
Cu(1)–Cl(3)	2.322(2)	Cu(2)–Cl(3)	2.325(2)
Cu(1)–Cl(2a)	2.242(2)	Cu(2)–Cl(1a)	2.709(1)
O(1)–Cu(1)–Cl(2a)	171.9(1)	O(1)–Cu(2)–Cl(1a)	98.7(1)
O(1)–Cu(1)–N(2)	82.3(2)	O(1)–Cu(2)–Cl(3)	82.2(1)
O(1)–Cu(1)–Cl(2)	101.7(1)	Cl(1)–Cu(2)–N(1)	98.2(1)
O(1)–Cu(1)–Cl(3)	81.6(1)	Cl(1)–Cu(2)–Cl(1a)	84.8(1)
Cl(2a)–Cu(1)–N(2)	96.6(1)	Cl(1)–Cu(2)–Cl(3)	95.8(1)
Cl(2a)–Cu(1)–Cl(2)	86.3(1)	Cl(1a)–Cu(2)–N(1)	96.6(1)
Cl(2a)–Cu(1)–Cl(3)	96.8(1)	Cl(3)–Cu(2)–N(1)	151.2(2)
Cl(2)–Cu(1)–N(2)	91.5(1)	Cl(1a)–Cu(2)–Cl(3)	109.7(1)
Cl(3)–Cu(1)–N(2)	155.9(1)	Cu(1)–Cl(2)–Cu(1a)	93.7(1)
Cl(2)–Cu(1)–Cl(3)	109.2(1)	Cu(1)–O(1)–Cu(2)	97.5(1)
O(1)–Cu(2)–Cl(1)	176.4(1)	Cu(1)–Cl(3)–Cu(2)	78.7(1)
O(1)–Cu(2)–N(1)	82.3(1)		

Table 3 Selected bond lengths (Å) and angles (°) for [{Cu(dpk)-(NO$_3$)$_2$}$_\infty$] 6

Cu(1)–O(20)	1.943(5)	Cu(1)–O(10)	2.015(5)
Cu(1)–N(1)	1.989(6)	Cu(1)–O(11)	2.339(6)
Cu(1)–N(2)	1.997(6)	O(11)–Cu(1a)	2.339(6)
O(20)–Cu(1)–N(1)	171.6(3)	N(2)–Cu(1)–O(11)	92.6(2)
O(20)–Cu(1)–N(2)	94.5(2)	O(10)–Cu(1)–O(11)	110.2(2)
N(1)–Cu(1)–N(2)	89.9(2)	N(3)–O(10)–Cu(1)	110.1(4)
O(20)–Cu(1)–O(10)	87.8(2)	N(3)–O(11)–Cu(1a)	113.7(5)
N(1)–Cu(1)–O(10)	90.8(2)	O(22)–N(4)–O(21)	125.3(8)
N(2)–Cu(1)–O(10)	157.1(2)	O(22)–N(4)–O(20)	118.4(7)
O(20)–Cu(1)–O(11)	83.5(2)	O(21)–N(4)–O(20)	116.4(7)
N(1)–Cu(1)–O(11)	89.2(2)	N(4)–O(20)–Cu(1)	117.5(5)

Table 1 Selected bond lengths (Å) and angles (°) for [{Cu$_2$[(NC$_5$-H$_4$)$_2$C(OEt)O]Cl$_3$(EtOH)}$_2$] 4

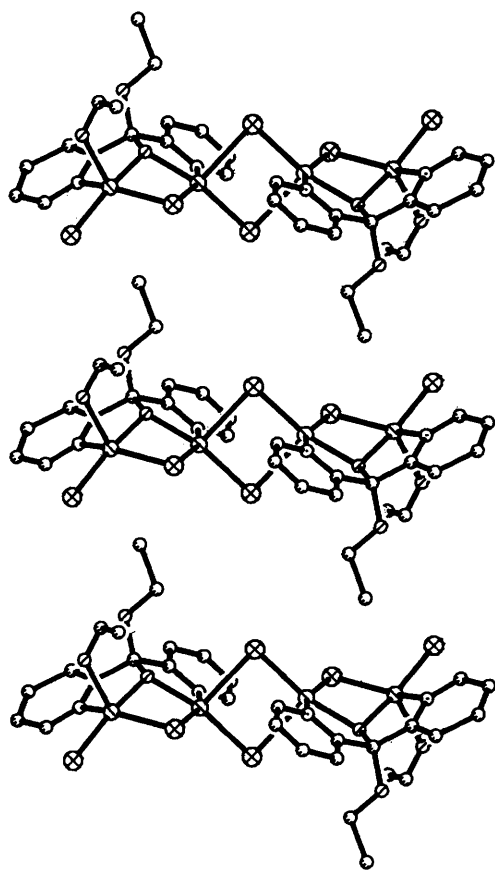|			
Cu(1)–O(1)	1.936(5)	Cu(2)–O(1)	1.936(5)
Cu(1)–N(1)	1.996(6)	Cu(2)–N(2)	2.006(7)
Cu(1)–Cl(1)	2.648(2)	Cu(2)–Cl(2)	2.333(3)
Cu(1)–Cl(2)	2.309(3)	Cu(2)–Cl(3)	2.228(3)
Cu(1)–Cl(1a)	2.258(2)	Cu(2)–O(3)	2.207(8)
O(1)–Cu(1)–Cl(1a)	168.1(2)	O(1)–Cu(2)–Cl(2)	81.6(2)
O(1)–Cu(1)–N(1)	81.5(2)	O(1)–Cu(2)–O(3)	93.0(3)
O(1)–Cu(1)–Cl(1)	101.1(2)	Cl(3)–Cu(2)–N(2)	98.3(2)
O(1)–Cu(1)–Cl(2)	81.6(2)	Cl(3)–Cu(2)–Cl(2)	96.1(1)
Cl(1a)–Cu(1)–N(1)	98.5(2)	Cl(3)–Cu(2)–O(3)	94.7(2)
Cl(1a)–Cu(1)–Cl(1)	98.4(2)	Cl(2)–Cu(2)–N(2)	148.8(2)
Cl(1a)–Cu(1)–Cl(2)	95.5(1)	O(3)–Cu(2)–N(2)	102.4(3)
Cl(1)–Cu(1)–N(1)	94.8(2)	Cl(2)–Cu(2)–O(3)	103.8(2)
Cl(2)–Cu(1)–N(1)	158.7(2)	Cu(1)–Cl(1)–Cu(1a)	89.5(1)
Cl(1)–Cu(1)–Cl(2)	101.2(1)	Cu(1)–O(1)–Cu(2)	101.1(1)
O(1)–Cu(2)–Cl(2)	170.3(5)	Cu(1)–Cl(3)–Cu(2)	81.5(1)
O(1)–Cu(2)–N(2)	80.9(3)		

Fig. 7 Packing of complex **4** viewed down the *c* axis showing the stacking of the pyridyl rings
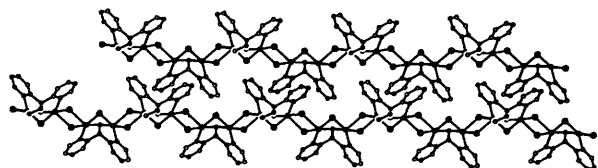

Fig. 8 Packing of complex **5** viewed down the *a* axis showing the zigzag stacking of the pyridyl rings
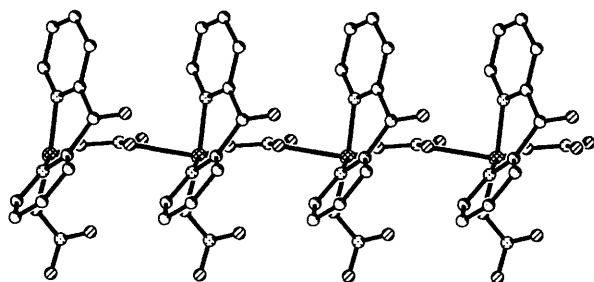

Fig. 9 Packing of complex **6** viewed down the *b* axis showing the one-dimensional chain structure

Magnetic behaviour

For the two halide-bridged systems very little variation of the magnetic moment with temperature is observed. Thus for compound **4** the moment per Cu is about 1.9 μ_B and nearly independent of T over the range 80–300 K, although it does show a slight increase as T is lowered with $\mu = 1.94 \mu_B$ at 80 K and 1.91 μ_B at 300 K. A similar trend is noted for **5**. For compound **6** the room-temperature moment is *ca.* 1.9 μ_B.

Overall the magnetic data for complexes **4** and **5** could be satisfactorily fitted using a Curie law which would seem to indicate that the copper centres do not interact. This non-interaction appears surprising in view of the relatively close
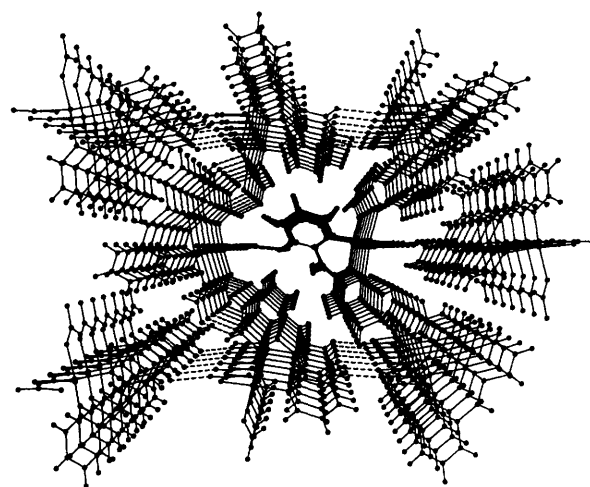

Fig. 10 Packing of complex **6** viewed down the *a* axis showing how the stacking of the chains results in the formation of channels

copper(II) centres. The treatment of Kahn *et al.*[11] to explain magnetic interactions in dinuclear $S = \frac{1}{2}$ systems requires consideration of the contributions of ferro- and antiferro-magnetic coupling (corresponding to the triplet and singlet state respectively). This approach can be extended to chains of N centres, with the case where N is infinite leading to a bistable system depending on whether N is odd (ferromagnetic) or even (antiferromagnetic). Such pairwise interactions can only occur if the magnetic orbitals on the metal centres are favourably aligned, and the parameters δ, τ and φ are a guide to this. For example, it has been shown for symmetrically dichloride-bridged copper pairs[5] that when δ and τ are zero ferromagnetic coupling occurs for $\varphi < 97.5°$, with the interaction becoming antiferromagnetic at angles greater than this. The effect of the twist angle τ is to give maximum ferromagnetic interaction at 30° and maximum antiferromagnetic interaction at 0 and 90°. The dihedral angle δ also has an effect on coupling which has not been quantified. Thus from the φ angles alone (Tables 1 and 2) the most significant coupling pathway would appear to be *via* Cl(2) in compound **4** and Cl(3) in **5**, the halide linkage within the asymmetrically bridged portion of both structures, and would be predicted to be ferromagnetic in nature. However, there may well be a competing effect from the τ angles, which in both compounds might be expected to give rise to antiferromagnetic coupling. The δ angles are probably not large enough to exert any great effect on any co-operative behaviour. It should be stressed that such arguments may not be directly applicable to these systems with the complication of the deprotonated hemiketal bridge, but it is possible that competing antiferro-and ferro-magnetic coupling pathways may be the origin of the apparent non-interaction of the copper centres and these are a consequence of the overall structure of the compounds. The alternative is that the copper centres actually are magnetically isolated. For example, this is reported to be the case for other copper chains such as dichlorobis(1,2,4-triazole)copper(II).[12] This complex and other related ones have μ_{eff} values of $\approx 1.8 \mu_B$ at room temperature suggesting there is no spin interaction. However low-temperature magnetic susceptibility studies on related complexes have shown that there is antiferromagnetic interaction between the copper atoms.[13] The resolution to this requires much more detailed magnetic studies on the compounds reported here, including experiments to determine the ground spin states, which are currently in progress.

Conclusion

The work described in this paper further serves to support the methodology of using ligand functionality to control the size and dimensionality of metal aggregates.[1] For example, we have

previously shown that the dinucleating mode of the alkoxide function of $N(CH_2CO_2H)_2(CH_2CH_2OH)$ was important in the construction of the polyiron hydroxide oxide clusters synthesized in this laboratory.[14] In the case of these clusters all the chelating groups of the ligand (with the exception of the dinucleating alkoxide) were bound to the same metal centre. This leads to the formation of two-dimensional structures. For compounds 4 and 5, where the dpk ligand is in its activated form, the dinucleating OH group and the chelating groups of the ligand bind to two different metal centres. In this way the activated dpk ligand favours the construction of one-dimensional systems. Interestingly, the hydrogen-bonding interactions between the tetramer units of compound 4 do not lead to the same overall packing as observed in the closely related infinite structure of 5, suggesting that the dictates of the dpk ligands are an important influence here. Compound 6 also forms a one-dimensional structure but this is a consequence of the bridging nitrate ligand since here the dpk is in its inactivated form and binds as a simple bidentate chelating ligand. In all cases the π–π interactions between the pyridyl rings of the ligand influence the crystal-packing arrangements, offering a further means of controlling the overall architecture and hence properties of the materials. Although the compounds reported here do not appear to display co-operative magnetic phenomena we have shown that the general synthetic strategy works. As we have stressed in the Introduction, our overall aim is to synthesize compounds which might, but not necessarily do, display pathways for the transfer of electronic information and to use the information gained from structural and magnetic studies to elucidate the factors important in achieving the objective. The information gained from the crystal structures points to ways to produce the desired magnetic interactions in future materials.[2,5,15] The further investigation of the magnetic behaviour and other properties of these compounds is currently in progress.

References

1 A. K. Powell and S. L. Heath, *Comments Inorg. Chem.*, 1994, **15**, 255.
2 R. D. Willett, *Coord. Chem. Rev.*, 1991, 181 and refs. therein.
3 R. E. Caputo, M. J. Vukosavovich and R. D. Willett, *Acta Crystallogr., Sect. B*, 1976, **32**, 2516.
4 R. D. Willett and U. Geiser, *Inorg. Chem.*, 1986, **25**, 4558.
5 R. D. Willett, R. M. Gaura and P. Landee, in *Extended Linear Chain Compounds*, ed. J. S. Miller, Plenum, New York, 1982, vol. 1, ch. 3, pp. 143–191 and refs. therein.
6 S.-L. Wang, J. W. Richardson, jun., S. J. Briggs, R. A. Jacobson and W. P. Jensen, *Inorg. Chim. Acta*, 1986, **111**, 67.
7 A. C. Deveson, A. Abufarag, M. B. Twitchet, M. Molinier, S. L. Heath, D. Harper, F. Mabbs, D. Collison and A. K. Powell, *Inorg. Chem.*, submitted for publication.
8 R. Baggio, O. González, M. T. Garland, J. Manzur, V. Acuña, A. M. Atria, E. Spodine and O. Peña, *J. Crystallogr., Spectrosc. Res.*, 1993, **23**, 749.
9 G. M. Sheldrick, SHELXTL PLUS, An integrated system for solving, refining and displaying crystal structures from diffraction data, Siemens Analytical X-Ray Instruments Madison, WI, 1990.
10 G. M. Sheldrick, SHELXL 93, Program for crystal structure determination, University of Göttingen, 1993.
11 O. Kahn, Y. Pei and Y. Journaux, in *Inorganic Materials*, eds. D. Bruce and D. O'Hare, Wiley, Chichester, 1995, ch. 2, pp. 60–114 and refs. therein.
12 M. Inoue, M. Kishita and M. Kubo, *Inorg. Chem.*, 1965, **4**, 626.
13 M. Inoue, S. Emori and M. Kubo, *Inorg. Chem.*, 1968, **7**, 1427.
14 A. K. Powell, S. L. Heath, D. Gatteschi, L. Pardi, R. Sessoli, G. Spina, F. Del Giallo and F. Pieralli, *J. Am. Chem. Soc.*, 1995, **117**, 2491.
15 R. L. Carlin, *J. Chem. Educ.*, 1991, **68**, 361.