Novel Monomeric and Dimeric Copper(II) Pyridone Complexes containing the 2,2′-Bipyridyl Ligand†

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The complexes $[\{Cu(chp)_2(bipy)\}_2]$ **1** and $[Cu(mhp)_2(bipy)]$ **2** have been prepared (chp = 6-chloro-2-pyridonate, mhp = 6-methyl-2-pyridonate, bipy = 2,2′ = bipyridine). Although both are monomeric in solution, **1** is dimeric in the solid state whereas **2** retains its monomeric structure. In the presence of water, **1** reacts to give a monomeric complex, $[Cu(chp)_2(bipy)(H_2O)]$ **3** which exhibits intramolecular hydrogen bonding. Reaction of **1** with $Cu(NO_3)_2{\cdot}3H_2O$ leads to partial substitution of the pyridone ligands, forming a second dimeric material, $[Cu_2(chp)_2(bipy)_2(H_2O)][NO_3]_2$ **4**. The crystal structures of **1**–**4** have been determined.

We have recently described[1–3] the preparation and reactivity of a series of copper(II) pyridone complexes. Although $[Cu_2(chp)_4]$[1] (chp = 6-chloro-2-pyridonate) and $[Cu_2(hp)_4(dmf)_2]$[4] (hp = 2-pyridonate, dmf = dimethylformamide) are isostructural with many other pyridone-bridged metal–metal multiply bonded complexes,[5] we were surprised to find that our attempts to prepare the analogous $[Cu_2(mhp)_4]$ (mhp = 6-methyl-2-pyridonate) complex yielded only the metallocrown, $[Cu_6(mhp)_{12}Na][NO_3]$.[2] In the presence of MeOH, $[Cu_2(chp)_4]$ forms a tetrameric structure,[6] $[Cu_4(OMe)_4(chp)_4]$, and an octameric structure,[6] $[Cu_8O_2(O_2CMe)_4(chp)_8]$ in the presence of $Cu_2(O_2CMe)_4{\cdot}2H_2O$. Other workers have recently reported other mixed copper–pyridone–carboxylate complexes.[7] The evident ability to form a large number of copper(II) pyridone complexes of varying nuclearity has led us to examine such complexes in the presence of chelating ligands. Such bidentate ligands should help satisfy the co-ordination requirement of each copper and thus induce the formation of stable low-nuclearity complexes. In a preliminary communication[6] we described the first of these complexes, $[\{Cu(chp)_2(bipy)\}_2]$ (bipy = 2,2′-bipyridine). We now report the full characterisation of this material and discuss its reactivity with water and copper nitrate. We also describe the structure of the complex of the methyl analogue, $[Cu(mhp)_2(bipy)]$, and discuss the possible importance of the position of the enolate/keto heteroaromatic tautomerism for these ligands.

Experimental

The complex $[Cu_2(chp)_4]$ was prepared according to the literature method.[2] The salts Na(mhp) and Na(chp) were prepared by reaction of Hmhp or Hchp respectively with Na in MeOH and dried *in vacuo*. Copper(II) hydroxide was freshly precipitated by the addition of aqueous NaOH to an aqueous solution of $CuCl_2{\cdot}2H_2O$ and filtered at a water pump. All solvents and other reagents were used as obtained: $CuCl_2{\cdot}2H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$ and NaOH (Fisons), Hmhp and Hchp, elemental Na and 2,2′-bipyridyl (Aldrich). Infrared spectra were recorded as Nujol mulls between KBr plates on a Perkin-Elmer 1600 series FTIR spectrometer, EPR spectra on a Brüker ER200D-SRC spectrometer.

Preparation of $[Cu_2(chp)_4(bipy)_2]$ **1**.—*Method* (*a*). The complex $[Cu_2(chp)_4]$ (0.641 g, 1 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and solid 2,2′-bipyridyl (0.312 g, 2 mmol) added with stirring. An immediate colour change from red to green was observed. Stirring was continued for 15 min to ensure complete reaction. Diffusion of Et_2O into this solution yielded many large, well formed green blocks over 24–48 h. Yield 0.4 g. Successive ether diffusions provided a total yield of 0.877 g, 92%. IR (cm^{-1}): 1587s(br), 1534m, 1522ms, 1450m, 1440m, 1379m, 1354w, 1335m, 1281w, 1254w, 1239w, 1217w, 1165w, 1150s, 1131s, 1104w, 1054m, 1030m, 1018w, 975vs, 914vs, 850w, 844w, 812w, 777vs, 765vs, 730s, 721s, 698vs, 660w, 652w, 635w and 601w (Found: C, 50.60; H, 3.00; N, 11.65. Calc.: C, 50.35; H, 2.95; N, 11.75%). FAB mass spectrum: *m*/*z* 696, $[Cu_2(chp)_2(bipy)_2]$; 668, $[Cu_2(chp)_3(bipy)]$; 568, $[Cu_2(chp)(bipy)_2]$; 540, $[Cu_2(chp)_2(bipy)]$; 503, $[Cu(chp)(bipy)_2]$; and 412, $[Cu_2(chp)(bipy)]$. UV/VIS (1.2×10^{-3} mol dm^{-3}, CH_2Cl_2): 14 245 ($\varepsilon = 103$), 24 391 (450) and 33 512 cm^{-1} (2.42×10^4 dm^3 mol^{-1} cm^{-1}). EPR (CH_2Cl_2, 298 K): $g = 2.143$, $a_{Cu} = 59.6$ G.

Method (*b*). The salt $Cu(NO_3)_2{\cdot}3H_2O$ (0.966 g, 4 mmol) and Na(chp) (1.212 g, 8 mmol) were ground together in a pestle and mortar to form a purple paste. 2,2′-Bipyridine (0.624 g, 4 mmol) was added and grinding continued to give a green paste [N.B. if the Na(chp) is rigorously dried, a few drops of CH_2Cl_2 assist the latter process]. The green paste was dissolved in CH_2Cl_2, filtered through Celite and recrystallised in a similar manner to that employed in method (*a*). Yield 1.64 g, 86%. This sample had elemental analyses, EPR and IR spectra comparable with those prepared by method (*a*).

$[Cu(mhp)_2(bipy)]$ **2**. This complex was prepared in a similar manner to **1** [method (*b*)]. Yield 79% IR (cm^{-1}): 1640m, 1610s, 1572m, 1548s, 1470s(br), 1398m, 1376s, 1313m, 1251w, 1220m, 1159s, 1109w, 1058w, 1042mw, 1030m, 1007m, 948w, 944w, 856m, 818w, 781vs, 748m, 732vs, 660w, 637w and 591w (Found: C, 59.55; H, 4.75; N, 12.75. Calc.: C, 60.60; H, 4.60; N, 12.85%). FAB mass spectrum: *m*/*z* 327, $[Cu(mhp)(bipy)]$; 219, $[Cu(bipy)]$; and 172 $[Cu(mhp)]$. EPR (CH_2Cl_2, 298 K): $g = 2.133$, $a_{Cu} = 70.1$ G.

$[Cu(chp)_2(bipy)(H_2O)]$, **3**. A saturated solution of complex **1** (0.2 g, 0.2 mmol) in CH_2Cl_2 was allowed to stand over an excess of freshly prepared $Cu(OH)_2$ for 3 d, producing well formed crystals of **3** amongst the excess of $Cu(OH)_2$. The solution was filtered and the precipitate dried on filter-paper. Crystals of **3** were isolated by Pasteur separation. Yield 0.03 g, 14%. IR (cm^{-1}): 3220s(br), 1593vs, 1525s, 1495m, 1443s, 1378m, 1356s, 1323w, 1310w, 1280w, 1265w, 1253w, 1221w, 1176w, 1157vs, 1061mw, 1031mw, 1016w, 984s, 950m, 911m, 864w, 858w, 785s, 765s, 729m, 704mw, 691w, 650w, 637w and 582w. FAB mass

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI units employed: G = 10^{-4} T, $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

spectrum: *m/z* 540, $[Cu_2(chp)_2(bipy)]$; 412, $[Cu_2(chp)(bipy)]$; 347, $[Cu(chp)(bipy)]$; and 219, $[Cu(bipy)]$. EPR (CH_2Cl_2): (298 K)$g = 2.118, a_{Cu} = 64.5$ G; (77 K)$g_1 = 2.071, g_2 = 2.019$ (Found: C, 48.55; H, 3.00; N, 11.30. Calc.: C, 48.55; H, 3.25; N, 11.35%).

$[Cu_2(chp)_2(bipy)_2(H_2O)][NO_3]_2\cdot Hchp\cdot H_2O$ **4**$\cdot Hchp\cdot H_2O$. A saturated solution of complex **1** (0.2 g, 0.2 mmol) in CH_2Cl_2 was allowed to stand over an excess of $Cu(NO_3)_2\cdot 3H_2O$ for 7d. The solution was decanted off and the dark green crystals of **4**$\cdot Hchp\cdot H_2O$ were isolated by Pasteur separation. Yield 0.01 g, 3% (Found: C, 41.20; H, 3.15; N, 12.55. Calc.: C, 42.00; H, 3.05; N, 11.35%). FAB mass spectrum: *m/z* 540 $[Cu_2(chp)_2(bipy)]$; 412, $[Cu_2(bipy)(chp)]$; 347, $[Cu(bipy)(chp)]$; 281, $[Cu(bipy)(NO_3)]$; and 219, $[Cu(bipy)]$.

Crystallography.—Crystal data and data collection and refined parameters for compounds **1**–**4** are given in Table 1, atomic coordinates in Table 2 and selected bond lengths and angles in Table 3.

Data collection and processing. Stoë Stadi-4 diffractometer, equipped with an Oxford Cryosystems low-temperature device[9] operating at 150 K with graphite-monochromated Mo-Kα radiation, ω–2θ scans. Data were corrected for Lorentz and polarisation factors. For complex **1** a correction for *ca.* 4% isotropic decay was applied.

Structural analysis and refinement. All structures were solved by the heavy-atom method, which revealed the positions of Cu atoms. All remaining non-hydrogen atoms were located from subsequent ΔF maps. For complex **1** all non-H atoms were refined anisotropically and H atoms were located in the difference map and refined freely. For **2** the Cu and pyridone non-H atoms were refined anisotropically, bipyridyl non-H atoms were refined isotropically, and H atoms were added at idealised positions (C–H 1.08 Å) with fixed $U_{iso} = 0.06$ Å^3. Two molecules of CH_2Cl_2 were located in a difference map, the chlorine atoms of which were refined anisotropically. One of these molecules showed two-fold disorder in the location of the carbon atom; the occupancy of the two positions at convergence was 47:53 with constrained thermal parameters. For **3**, the Cu, all pyridone non-H atoms and bipyridyl N atoms were refined anisotropically. The H atoms of the co-ordinated water were located in the difference map and refined freely; other H atoms were added at idealised positions as before. For **4** all non-H atoms except the bipyridyl C atoms were refined anisotropically. The H atoms of the bridging water molecule were located in the difference map and refined freely; other H atoms were added at idealised positions as before. A molecule of Hchp and a molecule of H_2O were located in a difference map and refined isotropically. Structure solution and refinement of all four structures were carried out using SHELX 76[10] and published scattering factors.[11]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results

Addition of 2 equivalents of bipy to a solution of $[Cu_2(chp)_4]$ in CH_2Cl_2 produced an immediate colour change from red to deep green. Ether diffusion into the resultant solution led to large well formed crystals of $[\{Cu(chp)_2(bipy)\}_2]$ **1** in 92% recovered yield. This complex can also be conveniently prepared, on a gram scale, by grinding $Cu(NO_3)_2\cdot 3H_2O$ with Na(chp) (1:2 mole ratio), followed by the addition of bipy (1 equivalent) to the resultant purple paste. It can be extracted with CH_2Cl_2 and recovered in a similar manner in overall 86% yield. In comparison, reaction of $Cu(NO_3)_2\cdot 3H_2O$ with Na(mhp) and bipy (1:2:1) in a similar fashion produced $[Cu(mhp)_2(bipy)]$, **2** in 79% recovered yield. Complexes **1** and **2** were characterised by infrared and mass spectrometry and provided satisfactory elemental analyses.

They are both EPR active in solution at room temperature and exhibit well defined quartet spectra (CH_2Cl_2) (**1**, $g = 2.143$, $a_{Cu} = 59.6$ G; **2**, $g = 2.133$, $a_{Cu} = 70.1$ G) similar to those observed for distorted square-planar CuN_4 complexes.[12] This is indicative of a mononuclear $CuL_2(bipy)$ (L = substituted pyridone) complex in solution, in which the copper(II) has an approximately square-planar environment of N atoms. No half-field resonance (caused by a triplet state arising through dimerisation) was observed in either sample. Although **2** was subsequently found to possess such a CuN_4 geometry in the solid state (see below), **1** does not and therefore must undergo a structural rearrangement on crystallisation. Complex **1** is EPR inactive in the solid state and exhibits a low effective magnetic moment ($\mu_{eff} = 1.1\ \mu_B$ per copper) whereas **2** retains its EPR-active behaviour and possesses a magnetic moment typical of an $S = \frac{1}{2}$ paramagnet. Such a contrast in properties can be explained in terms of the solid-state structures of **1** and **2**, determined by X-ray crystallography and illustrated in Figs. 1 and 2 respectively.

Complex **1** possesses two square-pyramidal copper atoms held together through two μ-pyridone oxygen bridges. The two copper (and oxygen) atoms are related through a crystallographic inversion centre and the resultant Cu_2O_2 ring is therefore planar. The short Cu $\cdots$ Cu distance [3.3295(4) Å] gives rise to an antiferromagnetic interaction between the copper centres leading to a low effective magnetic moment at room temperature. The nature of the copper–pyridone bridge is unprecedented, leaving both pyridone N atoms unco-ordinated, and consequently we can consider the pyridone anion to be co-ordinating purely in the enolate form. The oxygen bridges consist of long and short Cu–O bonds [1.942(2) and 2.339(2) Å respectively] and have associated Cu–O–Cu and O–Cu–O angles of 101.7(1) and 78.3(1)° respectively. Such μ-O-bonding

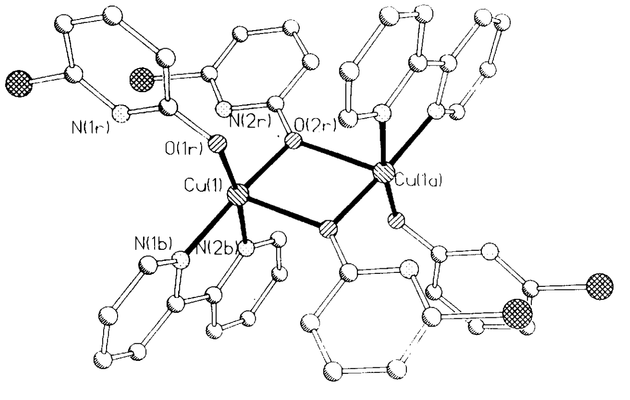

Fig. 1 Crystal structure of complex **1**

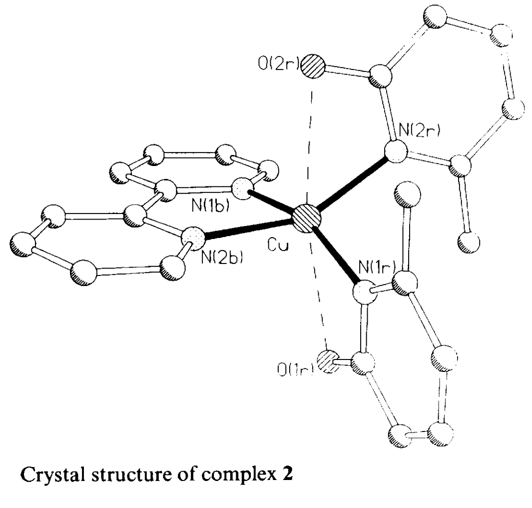

Fig. 2 Crystal structure of complex **2**

Table 1 Experimental data for the X-ray diffraction studies of compounds 1–4

Compound	1	2	3	4
Formula	$C_{40}H_{28}Cl_4Cu_2N_8O_4$	$C_{24}H_{24}Cl_4CuN_4O_2$	$C_{20}H_{16}Cl_2CuN_4O_3$	$C_{35}H_{30}Cl_3Cu_2N_9O_{11}$
M	953.6	605.8	494.8	986.1
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2/n$
a/Å	9.681(5)	10.020(8)	7.550(4)	11.164(5)
b/Å	9.786(5)	11.495(15)	16.150(8)	11.488(9)
c/Å	10.156(7)	11.661(8)	16.782(8)	16.102(13)
α/°	91.40(5)	84.15(4)	93.97(4)	90
β/°	91.61(5)	78.87(6)	94.24(5)	106.89(6)
γ/°	97.35(4)	85.91(8)	91.85(3)	90
U/Å^3	954	1309	2034	1976
Z	1^a	2	4^b	2^c
D_c/g cm^{-3}	1.66	1.54	1.62	1.66
F(000)	482	618	1004	1000
T/K	150.0(1)	150.0(1)	150.0(1)	150.0(1)
Crystal size/mm	0.47 × 0.35 × 0.31	0.25 × 0.25 × 0.01	0.66 × 0.47 × 0.23	0.25 × 0.15 × 0.07
Crystal colour, shape	Green block	Green plate	Green tablet	Dark green tablet
θ range/°	2.5–22.5	2.5–22.5	2.5–22.5	2.5–22.5
μ/mm^{-1}	1.454	1.276	1.369	1.352
Absorption correction	Yes^d	No	Yes^d	No
No. unique data	2423	3738	5313	2569
Observed data [$I_o > 2\sigma(I)$]	2238	1971	4722	1433
No. parameters	318	256	457	211
Maximum Δ/σ ratio	0.015	0.019	0.013	0.001
R,R'	0.0233, 0.0348	0.0893, 0.0944	0.0477, 0.0765	0.0689, 0.0782
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.000\,247F^2$	$\sigma^2(F) + 0.006\,457F^2$	$\sigma^2(F) + 0.000\,504F^2$	$\sigma^2(F) + 0.001\,404F^2$
Goodness of fit	1.236	1.066	1.181	1.056
Largest difference peak and hole/e Å^{-3}	+0.6, −0.4	+1.7, −1.6	+0.7, −0.9	+0.7, −1.1

[a] Molecule lies about an inversion centre. [b] Two molecules in the asymmetric unit. [c] Molecule lies on a crystallographic C_2 axis. [d] Absorption correction based on ψ scans.[8]

modes (where the N atom is unco-ordinated) have only previously been seen in complexes involving protonated pyridones, *e.g.* $[V_2O_2Cl_4(Hmhp)_3]$.[13] The co-ordination environment at each copper is thus composed of a long axial Cu–O(2r′) bond and four shorter bonds on the square base. Two of these bonds are to the chelating bipy ligand [Cu–N(1b) 2.010(2) and Cu–N(2b) 2.022(2) Å], one bond is the short 'equatorial' Cu–O(2r) and the final bond is to the second pyridone ligand. The latter is also unprecedented in that it is monodentate, binding only through O and leaving a donor N atom unco-ordinated. Again such a co-ordination mode is more usually observed in complexes of the neutral ligand where the protonated nitrogen is unable to act as donor group, *e.g.* $[Mn(Hmhp)_4][NO_3]_2$,[14] $[Fe(Hmhp)_6][NO_3]_2$,[15] $[Co(Hmhp)_4][NO_3]_2$[15] and $[Cu_2(O_2CMe)_4(Hhp)_2]$.[16] In many respects the structure is comparable to that of a dimeric copper complex containing protonated pyridone ligands, $[Cu_2Cl_4(Hhp)_4]$ **5**.[17] In **5** the two five-co-ordinate copper(II) centres are also bridged by two O atoms from protonated pyridones [$d_{Cu\cdots Cu}$ = 3.445(1) Å] and each have a second terminally bound monodentate pyridone. Two chloride anions take up the final two co-ordination sites. However, there is significant distortion away from the idealised square-based pyramidal structure, which may be caused by the intramolecular hydrogen bonding between bridging and terminal pyridone rings. The molecular packing of **1** is dominated by graphitic interactions between bipyridyl rings (*ca.* 3.5 Å) and Cl···Cl contacts (3.69 Å) between adjacent dimers.

Complex **2** is monomeric in the solid state and crystallises as a dichloromethane solvate, with copper at the centre of a compressed CuN_4 tetrahedron [N(1b)–Cu(1)–N(2b) 80.5(4), N(1r)–Cu(1)–N(2r) 98.3(4), N(1b)–Cu(1)–N(1r) 158.3(5) and N(2b)–Cu(1)–N(2r) 153.0(4)°] and longer contacts to the pyridone oxygen atoms (2.54 and 2.59 Å respectively) in the 'axial' positions (Fig. 2). The difference in co-ordination modes of the two pyridone ligands (chp and mhp) is marked. In **1**, chp is purely an O-donor whereas in **2**, mhp is chelating with a much stronger N-donor component. The mean pyridone C–O bond lengths in **2** [1.27(2) Å] are shorter than those in **1** [1.303(3) Å], consistent with a greater keto component to the bonding: this is highlighted in the IR (*cf.* ν_{CO} at 1587 cm^{-1} for **1** and 1610 cm^{-1} for **2**).

In comparison to $[Cu_2(chp)_4]$ which remains dimeric in dichloromethane solutions (unless in the presence of donor groups), complex **1** dissociates into discrete monomeric units. Consequently we undertook some investigations to see how the structure could be modified through the addition of further ligands.

When a saturated solution of complex **1** in CH_2Cl_2 was left to stand over an excess of freshly prepared $Cu(OH)_2$ for several days many well formed dark-green crystals appeared in and on the gel. These crystals were readily separated from the gel and characterised by elemental analysis, mass spectroscopy and a crystal structure as the monomeric complex, $[Cu(chp)_2(bipy)(H_2O)]$ **3**. There are two structurally similar molecules in the asymmetric unit, one of which is shown in Fig. 3. The co-ordination geometry about the copper(II) centre is a square-based pyramid. The CuN_2O_2 base is formed from the two bipyridyl nitrogens and the two pyridone oxygens, with Cu–N bonds in the range 2.007(4)–2.029(4) Å [mean 2.019(4) Å] and Cu–O bonds in the range 1.924(3)–1.945(3) Å [mean 1.934(4) Å]. The two pyridone rings are orientated towards the water molecule which takes up the apical position [mean Cu–O(w) 2.380(4) Å]. This crowding of the upper face is compensated for by O–H···N intramolecular hydrogen bonding between the co-ordinated water molecule and the pyridone N atoms [O–H 0.73(6)–0.88(6) and N···H 1.88–2.13(6) Å].

In a similar reaction, when a saturated solution of complex **1** in CH_2Cl_2 was left to stand over an excess of $Cu(NO_3)_2\cdot 3H_2O$ for 1 week a few dark green crystals of $[Cu_2(chp)_2(bipy)_2(H_2O)][NO_3]_2\cdot Hchp\cdot H_2O$, **4**·Hchp·$H_2O$, were formed. These

Table 2 Atomic coordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Complex **1**							
Cu(1)	0.068 92(3)	0.472 54(3)	0.854 88(3)	N(1r)	0.305 53(21)	0.290 19(21)	0.774 97(21)
N(1b)	0.163 33(21)	0.593 51(21)	0.718 14(20)	O(1r)	0.243 22(19)	0.437 71(19)	0.935 59(17)
C(1b)	0.299 8(3)	0.638 5(3)	0.717 2(3)	C(11r)	0.389 5(3)	0.198 8(3)	0.744 4(3)
C(2b)	0.357 0(3)	0.726 1(3)	0.623 6(3)	C(12r)	0.495 4(3)	0.159 0(3)	0.822 0(3)
C(3b)	0.270 8(3)	0.766 7(3)	0.525 0(3)	C(13r)	0.514 5(3)	0.222 0(3)	0.945 7(3)
C(4b)	0.129 9(3)	0.721 3(3)	0.524 4(3)	C(14r)	0.430 0(3)	0.316 0(3)	0.984 1(3)
C(5b)	0.078 1(3)	0.636 48(24)	0.623 98(24)	C(15r)	0.323 44(25)	0.349 5(3)	0.897 4(3)
C(6b)	−0.072 0(3)	0.588 46(24)	0.639 27(23)	Cl(2r)	−0.066 74(11)	−0.010 58(8)	0.649 44(7)
C(7b)	−0.176 4(3)	0.620 0(3)	0.554 7(3)	N(2r)	−0.061 65(22)	0.182 84(21)	0.831 92(20)
C(8b)	−0.313 0(3)	0.571 1(3)	0.579 7(3)	O(2r)	−0.038 85(18)	0.362 14(16)	0.981 76(16)
C(9b)	−0.341 5(3)	0.492 7(3)	0.689 6(3)	C(21r)	−0.104 6(3)	0.049 9(3)	0.807 3(3)
C(10b)	−0.231 8(3)	0.464 9(3)	0.770 4(3)	C(22r)	−0.168 5(3)	−0.042 1(3)	0.891 5(3)
N(2b)	−0.099 41(21)	0.510 48(20)	0.745 98(19)	C(23r)	−0.185 3(3)	0.008 0(3)	1.017 0(3)
Cl(1r)	0.358 84(9)	0.120 59(7)	0.586 32(7)	C(24r)	−0.141 2(3)	0.143 7(3)	1.049 7(3)
				C(25r)	−0.080 05(25)	0.231 26(25)	0.954 86(24)
Complex **2**							
Cu	−0.014 56(17)	0.292 75(14)	0.335 95(14)	C(4r)	−0.273 5(15)	0.535 7(13)	0.205 8(12)
N(1b)	0.017 6(10)	0.236 3(9)	0.496 7(10)	C(5r)	−0.186 7(14)	0.460 1(12)	0.272 9(12)
C(01b)	0.105 1(14)	0.278 1(12)	0.553 2(12)	C(6r)	0.005 4(15)	0.282 7(13)	0.043 1(13)
C(02b)	0.118 5(15)	0.235 6(12)	0.662 4(12)	N(2r)	0.174 7(10)	0.339 9(9)	0.273 5(9)
C(03b)	0.042 0(14)	0.144 9(12)	0.718 3(12)	C(21r)	0.247 3(14)	0.239 8(12)	0.236 4(12)
C(04b)	−0.050 6(14)	0.099 9(12)	0.663 5(12)	O(2r)	0.179 7(10)	0.146 2(8)	0.250 2(8)
C(05b)	−0.060 6(13)	0.147 7(11)	0.553 1(11)	C(22r)	0.371 9(13)	0.451 2(12)	0.205 4(11)
C(06b)	−0.159 0(14)	0.108 6(12)	0.483 6(12)	C(23r)	0.445 6(15)	0.352 5(12)	0.166 9(12)
C(07b)	−0.238 0(13)	0.016 5(11)	0.521 8(11)	C(24r)	0.386 6(14)	0.248 0(12)	0.184 0(12)
C(08b)	−0.327 6(14)	−0.012 7(12)	0.450 6(12)	C(25r)	0.235 5(15)	0.442 8(13)	0.259 8(12)
C(09b)	−0.332 6(14)	0.053 7(12)	0.346 5(12)	C(26r)	0.150 2(15)	0.545 8(12)	0.306 7(13)
C(10b)	−0.246 5(15)	0.146 7(12)	0.313 9(13)	Cl(11)	0.435 2(4)	0.759 9(4)	0.318 9(4)
N(2b)	−0.160 3(11)	0.172 3(9)	0.381 8(9)	Cl(12)	0.517 0(4)	0.675 1(4)	0.540 5(4)
O(1r)	−0.188 4(10)	0.461 8(8)	0.380 0(8)	C(1s)	0.428 7(19)	0.648 9(16)	0.431 9(15)
C(1r)	−0.093 3(15)	0.369 8(12)	0.097 9(12)	Cl(21)	0.677 5(6)	−0.111 3(5)	0.087 2(4)
C(2r)	−0.176 5(16)	0.442 7(14)	0.034 5(15)	Cl(22)	0.718 5(9)	0.128 5(6)	−0.022 6(7)
N(1r)	−0.103 6(12)	0.379 4(10)	0.214 4(9)	C(2a1)	0.678(4)	−0.003(4)	−0.039(4)
C(3r)	−0.263 4(16)	0.524 3(14)	0.090 7(14)	C(2b1)	0.789(4)	−0.016(3)	−0.021(3)
Complex **3**							
Cu(1)	0.402 62(7)	0.606 52(4)	0.111 69(3)	Cu(2)	0.129 38(7)	0.893 67(4)	0.597 28(3)
N(11b)	0.290 1(5)	0.491 7(3)	0.118 80(25)	N(21b)	0.147 7(5)	0.920 42(25)	0.482 07(24)
C(11b)	0.280 9(7)	0.451 5(3)	0.185 6(3)	C(21b)	0.090 5(6)	0.870 4(3)	0.417 9(3)
C(12b)	0.200 9(7)	0.373 2(3)	0.185 1(3)	C(22b)	0.118 4(7)	0.891 1(3)	0.341 0(3)
C(13b)	0.130 5(7)	0.334 3(3)	0.113 1(3)	C(23b)	0.202 1(7)	0.965 9(3)	0.330 2(3)
C(14b)	0.141 0(7)	0.376 0(3)	0.043 3(3)	C(24b)	0.262 3(7)	1.017 7(3)	0.397 4(3)
C(15b)	0.225 0(6)	0.454 3(3)	0.048 7(3)	C(25b)	0.236 0(6)	0.992 3(3)	0.471 7(3)
C(16b)	0.248 5(6)	0.501 3(3)	−0.022 8(3)	C(26b)	0.294 5(6)	1.042 0(3)	0.547 6(3)
C(17b)	0.188 5(7)	0.474 5(3)	−0.100 1(3)	C(27b)	0.382 1(7)	1.118 7(3)	0.551 6(3)
C(18b)	0.217 0(7)	0.525 1(3)	−0.160 7(3)	C(28b)	0.426 7(7)	1.160 3(3)	0.624 1(3)
C(19b)	0.305 4(7)	0.601 8(3)	−0.142 9(3)	C(29b)	0.383 8(7)	1.125 1(3)	0.693 2(3)
C(110)	0.363 4(6)	0.623 2(3)	−0.064 8(3)	C(210)	0.298 5(7)	1.047 3(3)	0.685 8(3)
N(12b)	0.338 5(5)	0.575 55(24)	−0.004 97(24)	N(22b)	0.256 3(5)	1.005 97(25)	0.614 45(24)
N(1r)	0.427 8(5)	0.805 08(25)	0.098 58(24)	O(3r)	0.098 8(4)	0.883 19(23)	0.709 47(20)
O(1r)	0.585 8(4)	0.686 36(21)	0.087 40(21)	N(3r)	0.389 0(5)	0.858 60(25)	0.744 37(24)
C(11r)	0.584 5(6)	0.766 0(3)	0.094 3(3)	C(31r)	0.218 2(6)	0.865 0(3)	0.763 9(3)
C(12r)	0.744 7(7)	0.814 7(3)	0.092 2(3)	C(32r)	0.175 2(6)	0.855 2(3)	0.843 3(3)
C(13r)	0.738 2(7)	0.899 1(3)	0.093 7(3)	C(33r)	0.306 8(7)	0.836 7(3)	0.899 8(3)
C(14r)	0.577 2(7)	0.938 8(4)	0.097 1(3)	C(34r)	0.482 1(7)	0.830 5(3)	0.879 2(3)
C(15r)	0.431 3(6)	0.887 8(3)	0.101 4(3)	C(35r)	0.511 3(6)	0.842 8(3)	0.802 1(3)
Cl(1r)	0.223 60(18)	0.932 21(9)	0.106 36(9)	Cl(3r)	0.726 47(16)	0.839 46(9)	0.769 75(9)
N(2r)	0.195 7(5)	0.649 96(25)	0.264 13(24)	N(4r)	0.099 8(5)	0.698 5(3)	0.601 81(24)
O(2r)	0.471 7(4)	0.622 46(23)	0.224 65(20)	O(4r)	−0.056 7(4)	0.810 88(21)	0.566 71(21)
C(21r)	0.367 3(6)	0.631 3(3)	0.281 6(3)	C(41r)	−0.055 6(7)	0.733 2(3)	0.582 7(3)
C(22r)	0.428 9(7)	0.623 1(3)	0.362 5(3)	C(42r)	−0.216 8(7)	0.684 6(3)	0.576 6(3)
C(23r)	0.314 6(7)	0.633 8(3)	0.421 8(3)	C(43r)	−0.209 1(8)	0.602 0(4)	0.590 0(4)
C(24r)	0.138 8(8)	0.651 3(3)	0.402 9(3)	C(44r)	−0.047 9(8)	0.566 0(4)	0.608 2(4)
C(25r)	0.089 2(7)	0.658 3(3)	0.323 4(3)	C(45r)	0.096 3(7)	0.619 1(3)	0.614 6(3)
Cl(2r)	−0.131 27(18)	0.676 59(10)	0.293 43(9)	Cl(4r)	0.306 63(20)	0.578 01(10)	0.638 33(9)
O(1w)	0.147 6(5)	0.688 6(3)	0.106 86(25)	O(2w)	0.383 6(5)	0.810 9(3)	0.584 55(24)

Table 2 (*continued*)

Atom	x	y	z
Complex **4**			
Cu	−0.204 46(13)	0.310 70(14)	0.356 86(9)
N(1b)	−0.072 7(9)	0.216 9(8)	0.443 2(6)
N(2b)	−0.313 6(8)	0.240 6(9)	0.421 0(6)
C(1b)	−0.436 4(11)	0.249 5(12)	0.401 2(9)
C(2b)	−0.505 7(12)	0.201 9(13)	0.449 7(8)
C(3b)	−0.442 8(13)	0.141 4(12)	0.523 9(9)
C(4b)	−0.316 0(13)	0.129 5(13)	0.545 9(10)
C(5b)	−0.252 6(10)	0.178 8(12)	0.493 4(8)
C(6b)	−0.115 9(11)	0.170 9(11)	0.507 0(8)
C(7b)	−0.033 6(12)	0.113 0(12)	0.576 6(9)
C(8b)	0.089 3(13)	0.103 2(12)	0.580 0(10)
C(9b)	0.129 2(13)	0.145 8(12)	0.514 2(9)
C(10b)	0.043 8(11)	0.205 6(12)	0.446 7(8)
Cl(r)	−0.175 5(4)	0.528 6(3)	0.470 70(22)
N(1r)	−0.314 3(8)	0.453 9(9)	0.320 2(6)
O(1r)	−0.421 8(7)	0.370 8(7)	0.191 6(5)
C(1r)	−0.402 7(10)	0.461 1(13)	0.241 1(8)
C(2r)	−0.466 9(12)	0.566 5(12)	0.217 3(9)
C(3r)	−0.439 5(12)	0.659 6(12)	0.272 4(10)
C(4r)	−0.351 5(12)	0.650 0(11)	0.352 9(9)
C(5r)	−0.292 8(11)	0.547 7(12)	0.372 7(8)
N(1)	0.476 5(11)	0.012 0(10)	0.713 8(7)
O(1)	0.471 3(8)	−0.072 0(8)	0.761 3(6)
O(2)	0.577 0(9)	0.063 0(9)	0.719 9(6)
O(3)	0.378 6(9)	0.044 9(9)	0.658 9(6)
O(1w)	−0.250 00(0)	0.178 0(11)	0.250 00(0)
Cl(1s)	0.080 1(9)	0.530 7(10)	0.052 2(6)
C(1s)	0.184 7(16)	0.528 9(17)	0.164 0(12)
C(2s)	0.210 1(17)	0.426 3(18)	0.206 3(12)
N(2s)	0.210 1(17)	0.426 3(18)	0.206 3(12)
C(3s)	0.219 1(18)	0.634 2(16)	0.207 0(11)
O(1s)	0.232 4(21)	0.316 3(23)	0.182 5(15)
O(2s)	0.245 5(21)	0.126 4(19)	0.286 5(14)

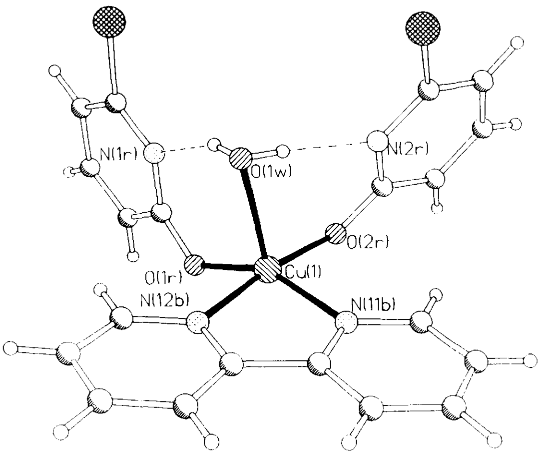

Fig. 3 Crystal structure of complex **3**

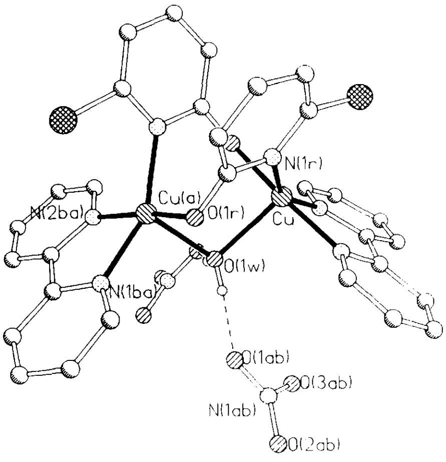

Fig. 4 Crystal structure of complex **4**

were separated by hand and characterised by elemental analysis and X-ray diffraction. The structure is shown in Fig. 4. It is composed of two Cu(bipy) fragments crystallographically related through a C_2 axis and triply bridged by two pyridone ligands and one water molecule. Unlike the parent complex **1**, the pyridone rings bridge the two copper(II) centres through an N,O donor set. The resultant Cu ··· Cu distance [3.293(2) Å] is slightly shorter than that found in **1** [3.3295(4) Å]. Each copper possesses a distorted square-pyramidal environment with a CuN_3O base composed of two bipyridyl N atoms [mean Cu–N 2.00(1) Å] and a N and an O from the bridging pyridone ligands. The mean deviation from the CuN_3O plane is 0.206 Å. The axially co-ordinated water [Cu–O(1w) at 2.244(7) Å] makes a Cu–O–Cu′ angle of 94.4°, whilst the angle between the two related CuN_3O planes is 85.9°. The bridging water is also hydrogen bonded to the two NO_3^- counter ions. The lattice also contains a disordered pyridone molecule and a second, non-co-ordinated, water molecule.

Discussion

The difference between the solid-state structures of complexes **1** and **2** is the second example we have found in copper co-ordination chemistry where similar synthetic routes using chp and mhp lead to quite different crystalline products. Previously it has been found[1,2] that the easily accessible homoleptic complexes of copper with these two ligands are $[Cu_2(chp)_4]$ and $[Cu_6(mhp)_{12}Na][NO_3]$. In that case, however, the differences observed in the crystal structures are reflected in the solution properties of the complexes which are clearly those of the specific oligomer.[3] The solution properties of **1** and **2** are surprisingly similar to each other and in both cases are consistent with the presence of monomeric species. However the difference between the solid-state structures remains to be explained.

There is little steric difference between the Cl and Me substituents, but it has long been known that the position of the tautomeric equilibrium in 2-pyridone derivatives depends on the nature of the electron-withdrawing/releasing group in the 6 position.[18] Thus the chp ligand should have a greater preference for the enol form than does the mhp ligand in which the keto form should predominate. It is tempting to explain the difference between complexes **1** and **2** in these terms as chp is bound exclusively through an exocyclic O atom in **1**, whilst mhp is bound primarily through the ring nitrogen. Variations in the C–O bond length and ν(C–O) also support this contention. The structure of **3** is also consistent with this argument. Unfortunately this electronic influence does not readily explain the difference between the $[Cu_2(chp)_4]$ and $[Cu_6(mhp)_{12}Na][NO_3]$ structures.

What is clear from the work reported here is that a wide range of structures are possible for copper with these ligands. Within the limited systems explored to date the copper co-ordination geometries vary from N_4 (in **2**) to N_3O_2 (in **4**) to N_2O_3 (in **1**

Table 3 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Complex **1**

Cu(1)–N(1b)	2.010(2)	O(1r)–C(15r)	1.293(3)
Cu(1)–N(2b)	2.022(2)	O(2r)–C(25r)	1.312(3)
Cu(1)–O(1r)	1.928(2)	Cu(1) ··· Cu(1a)	3.329(2)
Cu(1)–O(2r)	1.942(2)	Cu(1)–O(1r′)	2.339(2)
N(1b)–Cu(1)–N(2b)	80.10(8)	Cu(1)–O(1r)–C(15r)	127.63(17)
N(1b)–Cu(1)–O(1r)	93.04(8)	Cu(1)–O(2r)–C(25r)	119.68(15)
N(1b)–Cu(1)–O(2r)	174.49(8)	Cu(1)–O(2r)–Cu(1′)	101.70(7)
N(2b)–Cu(1)–O(1r)	171.88(8)	O(2r)–Cu(1)–O(2r′)	78.30(7)
N(2b)–Cu(1)–O(2r)	94.62(8)	O(1r)–Cu(1)–O(2r)	92.34(7)

Complex **2**

Cu–N(1b)	1.998(11)	Cu–O(1r)	2.540(10)
Cu–N(2b)	2.043(11)	Cu–O(2r)	2.598(9)
Cu–N(1r)	1.967(11)	C(21r)–O(2r)	1.291(16)
Cu–N(2r)	1.989(10)	O(1r)–C(5r)	1.248(17)
N(1b)–Cu–N(2b)	80.5(4)	N(1b)–Cu–N(1r)	158.3(5)
N(1b)–Cu–N(2r)	95.6(4)	N(2b)–Cu–N(1r)	94.1(4)
N(2b)–Cu–N(2r)	153.0(4)	N(1r)–Cu–N(2r)	98.3(4)
O(1r)–Cu–N(1b)	101.3(4)	O(1r)–Cu–N(2b)	92.1(4)
O(1r)–Cu–N(1r)	57.7(4)	O(1r)–Cu–N(2r)	114.7(4)
O(2r)–Cu–N(1b)	88.8(4)	O(2r)–Cu–N(2b)	95.7(4)
O(2r)–Cu–N(1r)	112.7(4)	O(2r)–Cu–N(2r)	57.4(4)
O(2r)–Cu–O(1r)	168.1(3)		

Complex **3**

Cu(1)–N(11b)	2.029(4)	Cu(2)–N(21b)	2.024(4)
Cu(1)–N(12b)	2.007(4)	Cu(2)–N(22b)	2.016(4)
Cu(1)–O(1r)	1.945(3)	Cu(2)–O(3r)	1.932(4)
Cu(1)–O(2r)	1.926(4)	Cu(2)–O(4r)	1.924(3)
Cu(1)–O(1w)	2.372(4)	Cu(2)–O(2w)	2.388(4)
O(1w)–H(1wa)	0.73(6)	O(2w)–H(2wa)	0.85(7)
O(1w)–H(1wb)	0.87(6)	O(2w)–H(2wb)	0.77(8)
N(11b)–Cu(1)–N(12b)	80.15(16)	N(21b)–Cu(2)–N(22b)	80.04(16)
N(11b)–Cu(1)–O(1r)	155.70(16)	N(21b)–Cu(2)–O(3r)	172.09(16)
N(11b)–Cu(1)–O(2r)	94.41(16)	N(21b)–Cu(2)–O(4r)	91.68(15)
N(11b)–Cu(1)–O(1w)	101.01(15)	N(21b)–Cu(2)–O(2w)	87.81(15)
N(12b)–Cu(1)–O(1r)	91.88(15)	N(22b)–Cu(2)–O(3r)	94.83(15)
N(12b)–Cu(1)–O(2r)	173.06(15)	N(22b)–Cu(2)–O(4r)	159.68(15)
N(12b)–Cu(1)–O(1w)	86.23(15)	N(22b)–Cu(2)–O(2w)	98.23(15)
O(1r)–Cu(1)–O(2r)	91.41(14)	O(3r)–Cu(2)–O(4r)	91.20(14)
O(1r)–Cu(1)–O(1w)	101.32(14)	O(3r)–Cu(2)–O(2w)	98.95(14)
O(2r)–Cu(1)–O(1w)	99.11(14)	O(4r)–Cu(2)–O(2w)	99.97(14)
Cu(1)–O(1w)–H(1wa)	94.7(50)	Cu(2)–O(2w)–H(2wa)	87.4(46)
Cu(1)–O(1w)–H(1wb)	78.5(39)	Cu(2)–O(2w)–H(2wb)	91.0(58)
H(1wa)–O(1w)–H(1wb)	99.5(64)	H(2wa)–O(2w)–H(2wb)	102.3(74)

Complex **4**

Cu–N(1b)	2.017(10)	Cu–N(2b)	1.983(10)
Cu–N(1r)	2.035(10)	Cu–O(1w)	2.244(7)
O(1w)–H(1w)	0.820(10)		
N(1b)–Cu–N(2b)	81.9(4)	N(1b)–Cu–N(1r)	152.8(4)
N(1b)–Cu–O(1w)	97.1(3)	N(2b)–Cu–N(1r)	94.0(4)
N(2b)–Cu–O(1w)	95.0(3)	N(1r)–Cu–O(1w)	110.1(3)
Cu–O(1w)–H(1w)	112.6(8)		

and 3). The ligands are found to be monodentate (bound through O only) in complexes **1** and **3**, or N bound (in **2**) or bridging through an oxygen (in **1**) or 1,3-bridging (in **4**).

The structure of complex **4** is particularly interesting. The copper co-ordination planes are approximately mutually orthogonal and in principle such derivatives should exhibit a ferromagnetic interaction.[19] The complex also bears a passing resemblance to the active site of the copper-containing oxygen carrier haemocyanin[20] although we have yet to displace the bridging water molecule with peroxide. Studies of the magnetic properties of the four complexes reported here, and of other pyridone complexes we have previously reported, are underway and will be the subject of a future report.

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