Copper(II) Bipyridyl and Iminopyridyl Analogues of Streptonigrin†

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The crystal structures of (3-amino-6,6′-dimethyl-2,2′-bipyridine)dichlorocopper(II) [CuL^1Cl_2], and aqua[3-imido-6-(methoxycarbonyl)-2,2′-bipyridine-6′-carboxylato]copper(II), [$CuL^3(H_2O)$], have been determined. The complex [CuL^1Cl_2] crystallizes in space group *Pnma* with $a = 19.434(3)$, $b = 7.427(2)$, $c = 9.403(1)$ Å and $Z = 4$. The structure has been refined to a final R value of 0.057 based on 680 independent reflections. The copper(II) centre exhibits tetrahedral co-ordination to the bipyridyl nitrogens of L^1 and two chlorine atoms. Crystals of [$CuL^3(H_2O)$] were grown from a solution of 3-amino-6,6′-bis(methoxycarbonyl)-2,2′-bipyridine (L^2) and excess Cu^{II}. The complex crystallizes in space group $P2_1/n$ with $a = 3.724(2)$, $b = 14.375(3)$, $c = 22.953(5)$ Å, $\beta = 90.72(3)°$ and $Z = 4$. The structure has been refined to a final R value of 0.061 based on 944 independent reflections. The Cu^{II} centre is square planar with a slight tetrahedral deformation, and co-ordinates to an imino nitrogen, adjacent pyridyl nitrogen, carboxylate oxygen and a water molecule. The implications of these results on the types of complexes formed by streptonigrin are discussed.

Streptonigrin is an aminoquinone antibiotic with antiviral[1] and anticancer properties.[2] Rings A, B and C and the substituents on these rings are essential for cytotoxic activity[3] which is believed to be related to the drug's ability to cause DNA strand scission in a redox cycle that generates radicals in the presence of oxygen.[4-6] Divalent metal ions copper(II) and iron(II) were shown to accelerate streptonigrin-induced DNA strand scission,[7-9] and stable streptonigrin–metal–DNA complexes with zinc(II) and manganese(II) have been reported.[10] While several metal ions have been shown to bind to streptonigrin[11] no structural characterisation of any of its metal complexes has been reported, and the exact role of the metals ions in DNA strand scission and/or toxicity mechanisms is not clear.

On the basis of UV titration experiments in aqueous acetonitrile, Hajdu and Armstrong[12] proposed that Cu^{II} and Zn^{II} form two structurally different types of 1:1 complexes with streptonigrin (Scheme 1). They suggested that a harder metal ion such as Zn^{II} may be bound to the bipyridyl system and the carboxylate of ring C, whereas a relatively soft metal ion such as Cu^{II} may bind with the amine nitrogen of ring C and the pyridyl nitrogen of ring B. As formation of each of these complexes is accompanied by the release of one mol of protons,[13] we suggested that both complexes are likely to be bipyridyl complexes which form by release of one mol of protons from ring C pyridyl nitrogen, due to the zwitterionic nature of streptonigrin in polar solvents.[13]

Our studies have focused on the characterization of the solution structure(s) of the metal complexes of streptonigrin in order to establish the role of metal ions in the mechanism of its action. In this context, we have reported the synthesis and solution structures of the metal complexes of two models of the central metal binding site in streptonigrin, 3-amino-6,6′-dimethyl-2,2′-bipyridine (L^1)[14] and 3-amino-6,6′-bis(methoxycarbonyl)-2,2′-bipyridine (L^2).[15] Due to the paramagnetic nature of Cu^{II}, NMR spectroscopy could not be used to characterize the Cu^{II} complexes of these ligands. In the present paper, we report the solid-state structure of the Cu^{II} complexes of L^1 and 3-imido-6-(methoxycarbonyl)-2,2′-bipyridine-6′-carboxylate (L^3), which was formed *in situ* from metal-ion promoted hydrolysis of L^2.

Results

Addition of 1.0 equivalent of copper(II) chloride to L^1 gave the 1:1 complex [CuL^1Cl_2] **1**, which was fully characterized. Crystals suitable for diffraction were grown from a solution of **1** with excess copper(II) chloride (Table 1). An ORTEP[16] diagram of the complex is presented in Fig. 1 and shows L^1 acting as a bipyridyl ligand. Selected bond angles and distances are given in Table 2. Complex **1** exhibits a compressed tetrahedral co-ordination sphere (Fig. 1 and Table 2) which is not surprising given the fact that Cu^{II} complexes do not adopt regular tetrahedral geometries. The Cl(1)–Cu–N(2)–C(6) torsion angle of 62.2(3)° is typical of chelated tetrahedral Cu^{II} complexes.[17] The geometrical details contained in Table 2 are also unremarkable. The complexes are π stacked on the (0,1/4,0) and (0,3/4,0) mirror planes with a separation of 3.71 Å, half the length of the a axis, and an offset of 1.5 Å between paired complexes (Fig. 2). The packing of the complexes provides cavities that accommodate the chlorine atoms. The unique chlorine atom of complex **1** was found to be surprisingly disordered and was accordingly modelled with three distinct sites. The chlorine disorder may be associated with bipyridyl disorder about the mirror plane, which is suggested by the thermal ellipsoids of the ligand. Several contacts of less than 3.0 Å suggest that the chlorine disorder is driven by hydrogen bonding to neighbouring complexes.

Attempts to grow crystals of the Cu^{II}–L^2 complex from mol equivalents of L^2 and copper(II) chloride in water only gave crystals of L^2 suggesting that the formation constant of the Cu^{II}–L^2 complex in water is low. Hence excess copper(II) chloride was added to an aqueous solution of the Cu^{II} complex of L^2 to afford brown crystals of [$CuL^3(H_2O)$] **2**, the 1:1 complex formed by the monoester and Cu^{II}.‡ Fig. 3 shows

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.
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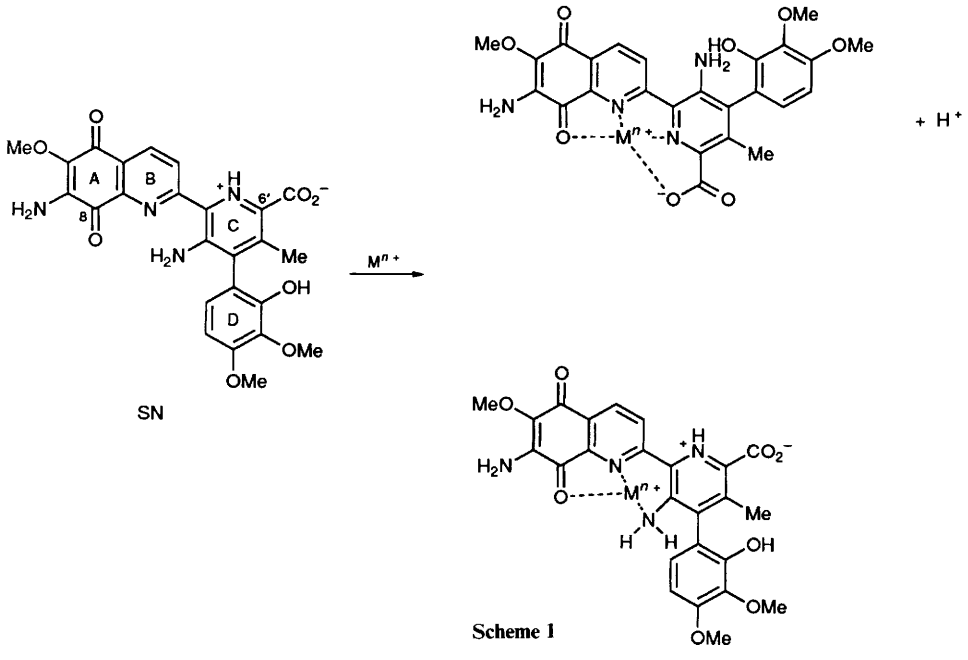
‡ Attempts to isolate larger amounts of [$CuL^3(H_2O)$] for further characterisation resulted in mixtures of complex **2** and the dihydrolysed complex [CuL^5].

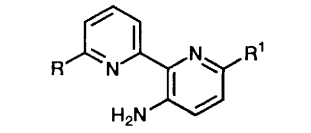
Table 1 Crystallographic details for the structures

	$[CuL^1Cl_2]$	$[CuL^3(H_2O)]$
Formula	$C_{12}H_{13}Cl_2CuN_3$	$C_{13}H_{11}CuN_3O_5$
M	333.71	352.79
T/K	294	294
Space group	*Pnma* (no. 62)	$P2_1/n$ (no. 14)
a/Å	19.434(3)	3.724(2)
b/Å	7.427(2)	14.375(3)
c/Å	9.403(1)	22.953(5)
β/°	—	90.72(3)
U/Å^3	1357.2(4)	1228.7(6)
D_c/g cm^{-3}	1.63	1.907
Z	4	4
μ/mm^{-1}	5.76	2.83
λ/Å	1.5406	1.5406
Minimum, maximum transmission	0.568, 0.895	0.94, 0.97
Reflections (independent, observed)	1222, 680 [$2.5\sigma(F)$]	1715, 944 [$2.0\sigma(F)$]
No. of variables	114	206
Residual/e Å^{-3}	−0.68 to 0.51	−0.75 to 0.70
R, R'[a]	0.057, 0.055	0.061, 0.061

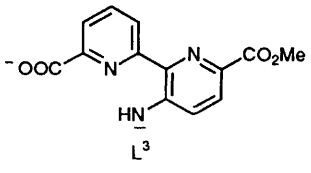
[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w = 1/\sigma^2(F)$.



Scheme 1



	R	R^1
L^1	Me	Me
L^2	CO_2Me	CO_2Me
L^4	CO_2^-	CO_2Me
L^5	CO_2^-	CO_2^-



L^3

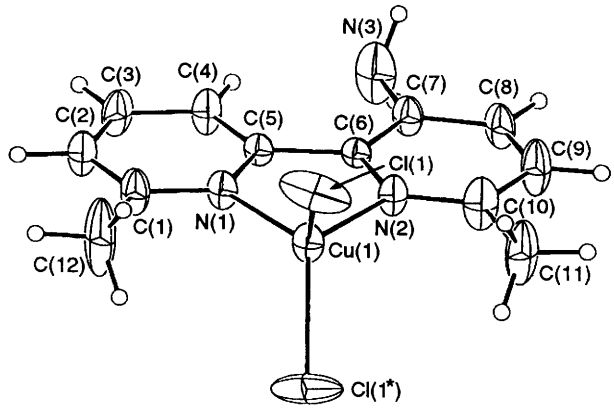


Fig. 1 An ORTEP representation of $[CuL^1Cl_2]$ with thermal ellipsoids plotted at the 25% level. The metal atom and ligand reside on a mirror plane. The Cl(1*) site is related to Cl(1) by the reflection x, $\frac{1}{2} - y$, z

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Cu–Cl(1)	2.273(8)	Cu–N(2)	1.964(8)
Cu–N(1)	1.967(8)		
Cl(1)–Cu–Cl(1)	103.3(4)	Cl(1)–Cu–N(2)	117.5(2)
Cl(1)–Cu–N(1)	118.4(3)	N(1)–Cu–N(2)	81.9(3)

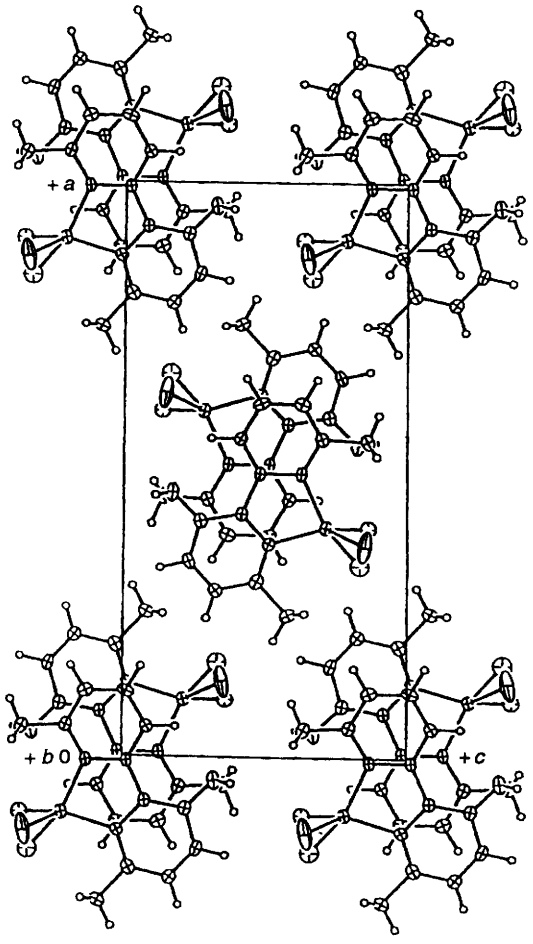


Fig. 2 An ORTEP representation of the unit cell of $[CuL^1Cl_2]$. The chlorine atom occupies a cavity and is disordered over three sites

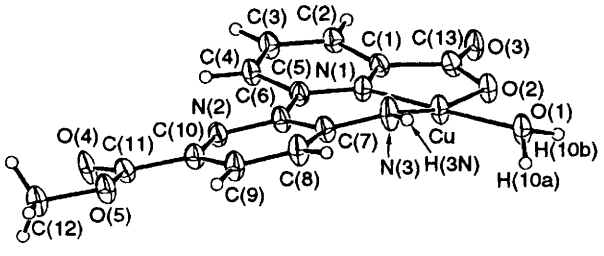


Fig. 3 An ORTEP representation of $[CuL^3(H_2O)]$ with thermal ellipsoids plotted at 25% probability

an ORTEP view of the structure in which L^3 is co-ordinated to the metal centre as a carboxylatepyridyl ligand assisted by the imino group* at the 6′ position. The complex is square planar with a slight tetrahedral deformation, with the O(1)–Cu–N(1) angle 176.1(3)° and O(2)–Cu–N(3) 169.2(4)° (Table 3). The copper sits 0.080 Å below the least-squares plane defined by O(1)–O(2)–N(1)–N(3), O(1) is 0.074 Å below this plane, N(1) is 0.074 Å below, O(2) is 0.056 Å above and N(3) is 0.11 Å above the plane. The molecules of complex **2** are π stacked polymerically with a copper–copper separation of 3.72 Å (the length of the *a* axis, see Fig. 4).

The complex was initially modelled as an aminopyridyl complex *i.e.* with ligand L^4. However, the non-hydrogen contacts with O(1) strongly suggest the presence of two attached protons (see Table 3), and the lattice is also supported by the hydrogen-bonding network depicted in Fig. 5. Furthermore, the sp^3 hybridised N(3) amino model has an amine proton 2.0 Å away from the copper of an adjacent complex which is highly unlikely. The independent Cu–N(3) distance of 1.877 Å is a little short, but is not unusual for an imine-co-ordinated copper complex,[18] but is unusually short for amine–copper complexes. Adopting an amine model would require an hydroxo complex and although not unknown,[19] such complexes are rare.

The formation of complex **2** from a solution of L^2 and excess copper(II) is clear evidence for metal-ion promoted hydrolysis of the ester group on the pyridyl ring not containing the amino group. This result is not unexpected; many examples of metal-ion promoted hydrolysis of esters containing chelating functional groups ($M = Mn^{II}$, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}) have been reported.[20] The selective hydrolysis of the 6′-ester may be rationalized as an electronic effect of the amino substituent on the ligand. Hydrolysis of both ester groups was observed on heating an aqueous solution of L^2 with copper(II) chloride, giving $[CuL^5]$ **3**.

Discussion

Streptonigrin contains many potential chelation sites including the pyridinecarboxylic acid system, the 2,2′-bipyridyl system, the aminoquinone system, the 2-(3′-amino-2′-pyridyl)quinoline system and the amino and phenolic groups on rings C and D. The structure(s) of the metal complexes of streptonigrin may influence the drug's activity in several ways. First, co-ordination may affect the reduction potential of the amino-quinone ring and hence the rate of production of semiquinone and other oxygen radicals. Secondly, metal complexation of streptonigrin (or reduced streptonigrin) may enable the drug to interact more strongly with DNA owing to changes in its structure or electronic character.[11,21] Finally, the metal ions may also participate in redox cycles involving streptonigrin, superoxide and production of hydroxyl radicals.[5–7,22]

Compounds L^1 and L^2 contain the amino group and the bipyridyl co-ordination subunit of streptonigrin. In addition, L^2 contains carbonyls at the 6,6′ positions as ester derivatives. For comparison, streptonigrin contains a carbonyl at the 8 position (ring A) of the quinone ring, and a carboxylate group at the 6′ position of ring C. The 6,6′-dicarboxylic acid (L^5) was also prepared as a model containing the carboxylate group present in streptonigrin, but was of limited use owing to the poor solubility of both the acid and complexes in a range of solvents. We showed previously that, in solution, both L^1 and L^2 bind Zn^{II} as bipyridyl ligands in organic solvents with no evidence of co-ordination of the amino nitrogen.[14,15] The 6,6′ ester groups in L^2 stabilized the 1:1 (ligand:metal) complex, whereas L^1 formed the 2:1 complex almost exclusively, even in the presence of excess Zn^{II}.[15]

The results of this study using Cu^{II} emphasize the influence of the carbonyl groups at the 6,6′ positions in determining the type of complexes formed by 3-amino-2,2′-bipyridyls. The compound L^1 formed the bipyridyl complex **1**, with no evidence of Cu^{II} binding to the amino group. Copper(II) is a borderline hard Lewis acid that tends to favour σ-donor ligands. Maximum overlap of the donor orbitals of the bipyridine ligand with the metal orbitals requires coplanarity of the pyridyl rings; L^1 then

* While not formally an imine functional group, the term imino group is used in the text to describe the co-ordination of the deprotonated amino group in L^3.

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

Cu–O(1)	1.987(7)	Cu–N(3)	1.877(9)
Cu–O(2)	1.943(7)	N(3)–C(7)	1.35(1)
Cu–N(1)	1.963(7)	H(10a)···O(3)*	1.9
O(1)–H(10a)	0.8	H(10b)···O(4)*	2.3
O(1)–H(10b)	1.0	H(3N)···O(3)*	2.4
N(3)–H(3N)	0.9	O(1)···O(4)*	2.775(9)
O(1)···O(3)†	2.66(1)		
N(3)···O(3)†	3.26(1)		
O(1)–Cu–O(2)	92.5(3)	O(2)–Cu–N(1)	83.7(3)
O(1)–Cu–N(1)	176.1(3)	O(2)–Cu–N(3)	169.2(4)
O(1)–Cu–N(3)	91.9(4)	N(1)–Cu–N(3)	91.9(3)
O(1)–H(10a)···O(3)	158	N(3)–H(3N)···O(3)	164
O(1)–H(10b)···O(4)	109		

* Estimated hydrogen bond, see Fig. 5. † Contact.

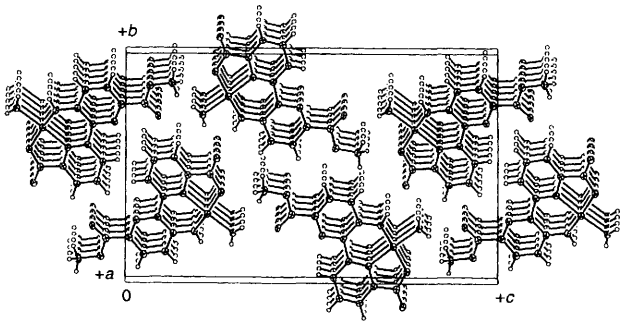


Fig. 4 An ORTEP projection down the *a* axis through four unit cells showing the nature of the stacking in the complex $[CuL^3(H_2O)]$

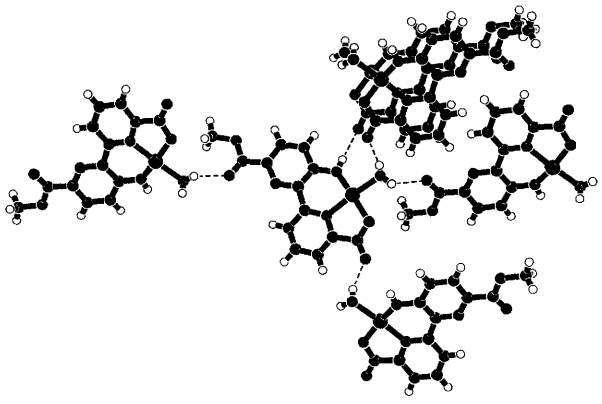


Fig. 5 Depiction of the hydrogen-bonding network in the crystal lattice of $[CuL^3(H_2O)]$

co-ordinates as a bipyridyl ligand as the alternative pyridyl–metal–amino co-ordination is disfavoured because of short metal–nitrogen distances and restricted angular overlap. This is contrary to the argument put forward by Hajdu and Armstrong[12] as an explanation for the differing spectroscopic properties of the Zn^{II} and Cu^{II} complexes of streptonigrin.

Treatment of L^2 with excess Cu^{II} resulted in the formation of the iminopyridyl complex **2**; selective hydrolysis of the 6′ ester may be rationalized as an electronic effect of the amino substituent on the ligand. In compound L^3 the donor orbital geometry of the pyridyl nitrogen and carboxylate oxygen is similar to that provided by the two bipyridyl nitrogens. The borderline hard Lewis acid copper(II) preferentially co-ordinates with the carboxylate oxygen to give the iminopyridyl–carboxylate complex **2**. The Cu, O(1), O(2) and N(1) atoms are coplanar (Fig. 3) with deviations of 0.0001, 0.001, 0.0001 and 0.001 Å respectively. In contrast the imine nitrogen N(3) is 0.32 Å above this plane, and this displacement is associated with a pyridyl–pyridyl dihedral angle of 15.18°. Presumably the deviation from square planar copper co-ordination reduces the Cu–N(3) electrostatic repulsion without undermining bond overlap. A simple calculation suggests that if the imine nitrogen did reside in the Cu–O(1)–O(2)–N(1) plane, the Cu–N(3) distance would be 1.849 Å, rather than the observed 1.877(9) Å. It is significant that it is N(3) that is displaced out of the copper co-ordination plane. The imine co-ordination found in complex **2** probably only occurs following pre-co-ordination to the carboxylate–pyridyl bidentate template. The observed Cu–N(3) distance of 1.877(9) Å is a little short for a copper–imine bond and is certainly too short comfortably to accommodate a copper–amine bond. It is however possible that a more distant initial amine co-ordination to copper triggers the release of an amine proton and hence the formation of the imine.

The crystal structures of complexes **1** and **2** reinforce the role of co-ordinating groups at the 6 and 6′ positions of 3-amino-2,2′-bipyridines in determining the types of complexes formed with metal ions. While L^4 (and L^3) contains a different substitution pattern from streptonigrin, the results of this study are relevant to the interaction(s) of metal ions with streptonigrin. In particular, they suggest that copper(II) will form a strong chelate with the carboxylate and pyridyl nitrogen in ring C. Formation of this chelate will preclude binding of the amino group and favour bipyridyl co-ordination of both copper(II) and zinc(II). The implications of the co-ordination geometry on the mechanism of action of streptonigrin are not obvious, and will require further characterization of the chemical and electrochemical properties of streptonigrin–metal complexes both in the presence and absence of DNA.

Experimental

Melting points were determined on a Reichert heating stage and are uncorrected. Ultraviolet spectra were recorded on a Hitachi 150-20 spectrophotometer. Electrospray (ES) mass spectra were recorded at the University of Wollongong on a Fisons/VG Quattro mass spectrometer; samples were introduced in MeCN–water (1:1) at 3–5 μl min^{-1}. The NMR spectra were recorded on a Bruker AMX400 spectrometer. Compounds L^1 and L^2 were prepared as previously described.[14,15]

Syntheses.—$[CuL^1Cl_2]$ **1**. A solution of copper(II) chloride (2.36 mg, 0.02 mmol) in methanol (0.1 cm^3) was added to a solution of 3-amino-6,6′-dimethyl-2,2′-bipyridine (L^1) (3.5 mg, 0.02 mmol) in methanol (0.1 cm^3). The red-yellow solution was stirred for 15 min and filtered giving (3-amino-6,6′-dimethyl-2,2′-bipyridine)dichlorocopper(II) (**1**) as a green solid (3.0 mg, 51%), m.p. > 300 °C (Found: C, 43.30; H, 4.25; N, 12.35. Calc. for $C_{12}H_{13}Cl_2CuN_3$: C, 43.20; H, 3.90; N, 12.60%); ν_{max}(KBr disc) 3319m, 3225m, 1572w, 1496m, 1467m, 1384s, 1243w, 838w and 803w cm^{-1}; *m/z* (ES) 200.1 ($[L^1 + H]^+$, 100) and 461.3 ($[CuL^1_2]^+$, 28). A crystal of **1** suitable for X-ray crystallography was obtained by addition of copper(II) chloride (1 mg, 0.0074 mmol) to a solution of **1** (0.5 mg, 0.0015 mmol) in water (0.3 cm^3). The solution was suspended as droplets (15 μl) above a well of 2-methylpentane-2,4-diol.

$[CuL^3(H_2O)]$ **2**. A solution of L^2 (9.9 mg, 0.034 mmol) in acetone (15 cm^3) was added to a solution of copper(II) chloride (4.8 mg, 0.036 mmol) in acetone (5 cm^3), stirred for 15 min, and the solvents removed *in vacuo*. The pale green solid was suspended in diethyl ether, held at reflux for 2 h and filtered. Copper(II) chloride (2 mg, 0.015 mmol) was added to a solution of the green solid (2 mg) in water (0.5 cm^3), filtered, and allowed to stand giving a small brown crystal of **2** suitable for X-ray diffraction.

$[CuL^5]$ **3**. The compound L^2 (8.4 mg, 0.029 mmol) was added to a solution of anhydrous copper chloride (4.0 mg, 0.030 mmol) in water (2 cm^3). The solution was refluxed for 2.5 h, cooled and the resultant precipitate collected and washed successively with methanol, ethanol and chloroform. The solid

Table 4 Positional parameters for complex **1**

Atom	*x*	*y*	*z*
Cu(1)	0.100 03(8)	0.25	0.215 9(2)
Cl(1)	0.131 4(6)	0.490(1)	0.351 1(7)
Cl(2)	0.100 4(6)	0.461(2)	0.364(1)
Cl(3)	0.166(1)	0.445(3)	0.334(2)
N(1)	0.007 8(4)	0.25	0.129 5(8)
N(2)	0.128 4(4)	0.25	0.015 4(9)
N(3)	0.040 9(6)	0.25	−0.325(1)
C(1)	−0.051 9(6)	0.25	0.202(1)
C(2)	−0.112 7(6)	0.25	0.132(1)
C(3)	−0.113 6(5)	0.25	−0.012(1)
C(4)	−0.052 0(6)	0.25	−0.086(1)
C(5)	0.007 9(5)	0.25	−0.017(1)
C(6)	0.077 0(5)	0.25	−0.081(1)
C(7)	0.089 5(6)	0.25	−0.226(1)
C(8)	0.159 6(6)	0.25	−0.267(1)
C(9)	0.210 0(6)	0.25	−0.173(1)
C(10)	0.194 2(7)	0.25	−0.027(1)
C(11)	0.252 5(7)	0.25	0.083(1)
C(12)	−0.047 9(8)	0.25	0.361(1)
H(1N)	0.046 17	0.356 64	−0.385 88
H(2)	−0.156 03	0.25	0.185 13
H(3)	−0.157 51	0.25	−0.063 99
H(4)	−0.052 35	0.25	−0.190 23
H(8)	0.170 96	0.25	−0.368 59
H(9)	0.258 02	0.25	−0.205 19
H(11a)	0.297 01	0.25	0.033 97
H(11b)	0.249 42	0.358 81	0.141 73
H(12b)	−0.022 65	0.356 64	0.392 88
H(12a)	−0.094 58	0.25	0.400 48

Table 5 Positional parameters for complex **2**

Atom	*x*	*y*	*z*
Cu(1)	0.065 3(3)	0.186 97(6)	0.721 56(4)
O(1)	0.021(2)	0.267 5(3)	0.791 5(2)
O(2)	−0.188(1)	0.084 9(3)	0.758 3(2)
O(3)	−0.324(1)	−0.0649(3)	0.746 0(2)
O(4)	0.537(1)	0.253 9(3)	0.411 6(2)
O(5)	0.776(1)	0.391 9(3)	0.434 1(2)
N(1)	0.092(2)	0.100 8(3)	0.655 4(2)
N(2)	0.426(1)	0.223 8(3)	0.529 7(2)
N(3)	0.384(2)	0.270 5(4)	0.686 5(2)
C(1)	−0.036(2)	0.016 1(4)	0.668 4(3)
C(2)	−0.008(2)	−0.058 5(4)	0.630 7(2)
C(3)	0.130(2)	−0.042 1(4)	0.576 3(3)
C(4)	0.243(2)	0.044 6(4)	0.561 1(3)
C(5)	0.228(2)	0.117 6(4)	0.601 9(2)
C(6)	0.371(2)	0.211 4(4)	0.587 3(3)
C(7)	0.434(2)	0.281 9(4)	0.628 7(3)
C(8)	0.597(2)	0.365 7(4)	0.607 7(3)
C(9)	0.647(2)	0.378 2(4)	0.549 3(3)
C(10)	0.565(2)	0.304 5(5)	0.511 2(2)
C(11)	0.618(2)	0.310 5(5)	0.448 1(3)
C(12)	0.861(2)	0.406 5(5)	0.373 9(3)
C(13)	−0.189(2)	0.007 7(5)	0.728 6(3)
H(10a)	−0.07(2)	0.314(5)	0.788(3)
H(10b)	−0.159 82	0.240 57	0.816 38
H(3N)	0.46(2)	0.319(4)	0.704(3)

was dried under vacuum to give **3** as a green amorphous solid (4.6 mg, 50%), m.p. > 300 °C (Found: C, 44.90; H, 2.65; N, 12.45. Calc. for $C_{12}H_7CuN_3O_4$: C, 44.95; H, 2.20; N, 13.10%); ν_{max}(KBr disc) 3405s, 3343m, 3200s, 1660m, 1631s, 1594s, 1564m, 1471w, 1384s, 1349s, 1318m, 1246w, 1180w, 851w and 836w cm^{-1}; *m*/*z* (ES) 321.3 ([CuL^5 + H]$^+$, 100).

X-Ray Crystallography.—The structures of the two complexes were determined at 21 °C on a Rigaku AFC7R direct drive rotating anode diffractometer equipped with a copper target [λ(Kα) = 1.5406 Å] and a graphite monochromator. Crystallographic details are given in Table 1. The crystals were mounted on thin glass fibres with cyanoacrylate resin. Lattice parameters were determined from the setting parameters of 25 independent reflections. Intensity data were collected from the crystal of complex **1** with a scan width of 0.84 + 0.35 tan θ° for ω scans repeated up to 10 times at 8° min^{-1}. Data were collected for complex **2** with a scan width of 1.05 + 0.35 tan θ° for ω–2θ scans repeated up to 10 times at 32° min^{-1}. Stationary background counts were recorded on each side of the reflections. The intensities of three representative reflections were measured after every 150 reflections. Data reduction and the application of Lorentz-polarisation corrections were carried out using the TEXSAN structure determination software package.[23] The structure was solved by direct methods using SHELXS 86,[24] extended by Fourier-difference methods and refined with full-matrix least-squares minimisation. Neutral atom scattering factors and anomalous dispersion terms used were those incorporated in the TEXSAN package. Analytical absorption corrections to the data were made following the measurement and indexing of the faces of the very small green crystals of the two complexes. The non-hydrogen atoms were refined with anisotropic thermal parameters, whereas in general the hydrogen atoms were placed at calculated positions (C–H 0.97 Å).

Both amine and imine models were refined against the diffraction data collected from the small crystal of complex **2**. However the data did not permit an unequivocal distinction between the two models. Sites for the aqua H(10a) and H(10b) and imine H(3)N sites of the imine model were located following convergence, and the positions of H(10a) and H(3N) were then successfully refined. However thermal parameters for these protons could not be refined satisfactorily, consequently their significance is unclear. The crystallographically unique chlorine atom of complex **1** was found to be surprisingly disordered and was accordingly modelled with three distinct sites. Several contacts of less than 3.0 Å suggest that the disorder may be associated with hydrogen bonding to neighbouring complexes.

Labelled ORTEP[16] projections for the crystallographic models are presented in Figs. 1 and 3. Selected bond lengths and angles are given in Tables 2 and 3, and final atomic coordinates are listed in Tables 4 and 5.

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

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