Fig. 2. Stereoscopic crystal packing diagram of the 'wet' form structure showing the alternating layers of 5'-IMP and water channel in which the two Na ions (circles with thick lines) are embedded.

two 5'-IMP molecules A and B are directly linked together using four strong hydrogen bonds (2·65–2·74 Å) between the phosphates and the ribose O2' and O3' hydroxyls, forming an infinite network (Fig. 2). In the water channels, some loosely bound water molecules could occur and cause the sharp change in the diffraction quality of the crystal either by moving in or escaping from the lattice.

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Structure of Bis(di-2-pyridylamine)copper(I) Chloride

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Abstract. [Cu(C$_{10}$H$_9$N$_3$)$_2$]Cl, $M_r = 441 \cdot 40$, monoclinic, $P2_1/n$, $a = 9 \cdot 675$ (2), $b = 16 \cdot 838$ (3), $c = 12 \cdot 618$ (1) Å, $\beta = 105 \cdot 91$ (1)°, $V = 1976 \cdot 8$ Å^3, $Z = 4$, $D_m = 1 \cdot 482$, $D_x = 1 \cdot 48$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 12 \cdot 6$ cm^{-1}, $F(000) = 904$, $T = 294$ (1) K, $R = 0 \cdot 031$ for 2850 observed reflections. The Cu atom is in a distorted tetrahedral environment of four N atoms from two di-2-pyridylamine ligands, with an average Cu—N distance of 2·016 (2) Å. The geometries of the di-2-pyridylamine ligands are quite different. The dihedral angle between the pyridyl rings is 5·6 (4)° for one ligand and 16·7 (2)° for the other. The chloride counterions form hydrogen-bonded bridges between adjacent complexes.

Introduction. Dipyridylamine has received interest as a ligand due to its ability to stabilize five-coordinate copper(II) complexes. The flexibility of the molecule at the amine N atom is manifested in the wide range

of dihedral angles observed between the pyridyl rings (9·8–41·4°). Steric hindrance between ring H atoms prevents dipyridylamine from complexing in square-planar coordination without ligand distortion.

The structures of several copper(II) complexes with two bidentate ligands have been studied. The four-coordinate bis(dipyridylamine)copper(II) perchlorate, $[Cu(dpaH)_2](ClO_4)_2$ (Johnson, Beineke & Jacobson, 1971) exists in a distorted tetrahedral configuration with nearly planar dipyridylamine ligands (dihedral angle 9·8°). The chloride (Jensen & Jacobson, 1981; Jacobson & Jensen, 1986) and iodide (Johnson & Jacobson, 1973a) salts of these complexes are all five coordinate, with the halogen occupying the fifth coordination site. The two ligands are non-planar and not identical for these five-coordinate copper(II) complexes as shown by dihedral angles between the pyridyl rings of 18·2 to 37·5°. These dihedral angles are comparable to the 23° angle found in the structure of the lower-melting polymorph of the uncomplexed ligand (Johnson & Jacobson, 1973b).

Copper(I) complexes with one dipyridylamine ligand have been investigated as models of copper-containing plant hormone binding sites. Stable complexes with ethylene, propylene, acetylene and carbon monoxide have been prepared and characterized (Thompson & Whitney, 1984). The structure of bis(di-2-pyridylamine)copper(I) chloride was determined to investigate the effect of the change of oxidation state of the metal on the structure and distortion of the ligand.

Experimental. Single crystals of bis(di-2-pyridyl-amine)copper(I) chloride were obtained from the reaction of copper(I) chloride with a stoichiometric amount of di-2-pyridylamine in acetonitrile under a nitrogen atmosphere and recrystallized from methanol. The density was measured by flotation in aqueous zinc bromide. A red-orange elongated plate with approximate dimensions $0·30 \times 0·20 \times 0·10$ mm was mounted on an Enraf–Nonius CAD-4 diffractometer. Cell constants were determined from 25 reflections in the range $12 < \theta < 14°$. The space group was determined to be $P2_1/n$ from the systematic absences ($h0l$, $h + l \neq 2n$, $0k0$, $k \neq 2n$). The hkl data range from 0, 0, −15 to 11, 20, 14, $2\theta_{max} = 52·0°$. Three standard reflections collected every 50 min changed by 0·6%. 4259 reflections were collected (ω–2θ scans), of which 4019 were unique ($R_{int} = 2·0\%$) and were corrected for Lorentz and polarization effects. The data were corrected for absorption (relative transmission coefficients 0·863 to 0·998) and decay (0·97–1·03). The structure was solved using Patterson and Fourier methods. 2850 reflections having intensities greater than 3σ were used in the refinement of 307 parameters where

$\sum w(|F_o| - |F_c|)^2$ was minimized with weighting scheme $w = 4F_o^2/\sigma^2(F_o^2)$. The refinement converged with $R = 0·031$ and $wR = 0·050$; $(\Delta/\sigma) = 0·02$; $(\Delta\rho)_{max} = 0·25$ (5) and $(\Delta\rho)_{min} = -0·48$ (5) e Å^{-3}. In the final cycles, all non-H atoms were refined anisotropically and H atoms assigned isotropic temperature factors equal to 1·3 times the U_{eq} of the atom to which they are bonded. The scattering factors were taken from Cromer & Waber (1974) and anomalous-dispersion coefficients were those of Cromer (1974). All calculations were performed on a VAX11/750 computer using SDP/VAX (Frenz, 1978).*

Discussion. Table 1 contains the final positional and equivalent isotropic thermal parameters. The bond lengths and angles with standard deviations are in Table 2. The structure of the bis(di-2-pyridylamine)-copper(I) cation in an $ORTEP$ (Johnson, 1971) drawing with 30% thermal ellipsoids is shown in Fig. 1. The complex cation consists of a Cu^I atom in a highly distorted tetrahedral environment with two neutral di-2-pyridylamine ligands. The chloride counterion is not coordinated.

The Cu, N(1), N(3) plane intersects the Cu, N(4), N(6) plane at an angle of 73·27 (7)°, which is significantly smaller than that expected for regular tetrahedral coordination. The dihedral angle between the planes of the ligands in the tetrahedrally distorted perchlorate salt of the copper(II) complex is 55·6°, demonstrating that the coordination sphere of the copper does not undergo a major reorientation upon a change in oxidation state of the metal.

The two di-2-pyridylamine ligands are not related by symmetry and show distinct differences. The N—Cu—N angles for the di-2-pyridylamine ligands are 95·02 (7) and 93·71 (7)°. Although both ligands deviate from planarity, one ligand shows significantly more distortion than the other. The dihedral angles between the two pyridyl groups are 5·6 (4)° [N(1), N(3)] and 16·7 (2)° [N(4), N(6)], respectively, for the two ligands. The largest deviations from the least-squares plane for the pyridyl rings in the more-planar ligand are 0·022 (2) and 0·018 (2) Å. The largest deviation from planarity for atoms in the pyridyl rings in the more-distorted ligand are 0·031 (2) and 0·057 (2) Å. The geometry around the amine N atom in the complexed di-2-pyridylamine is virtually planar. The bond lengths and bond angles in the pyridyl rings are in agreement with the structure of the low-melting-point polymorph of di-2-pyridylamine.

BIS(DI-2-PYRIDYLAMINE)COPPER(I) CHLORIDE

Table 1. *Positional parameters and their e.s.d.'s*

B_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$B_{eq}/B_{iso}(Å^2)$
Cu	0.74157 (3)	−0.10104 (2)	0.74770 (2)	4.707 (7)
Cl	1.13524 (5)	0.14509 (3)	0.57608 (5)	3.91 (1)
N(1)	0.9470 (2)	−0.1042 (1)	0.7386 (2)	3.67 (4)
N(2)	0.9251 (2)	0.0157 (1)	0.6383 (1)	3.42 (4)
N(3)	0.6919 (2)	0.0003 (1)	0.6627 (1)	3.60 (4)
N(4)	0.6698 (2)	−0.1033 (1)	0.8836 (2)	4.08 (4)
N(5)	0.5409 (2)	−0.2235 (1)	0.8343 (1)	3.55 (4)
N(6)	0.6672 (2)	−0.2111 (1)	0.6989 (1)	3.62 (4)
C(1)	1.0284 (3)	−0.1687 (1)	0.7769 (2)	4.60 (5)
C(2)	1.1622 (3)	−0.1814 (2)	0.7652 (2)	4.94 (6)
C(3)	1.2197 (2)	−0.1243 (2)	0.7114 (2)	4.40 (5)
C(4)	1.1402 (2)	−0.0588 (1)	0.6699 (2)	3.63 (5)
C(5)	1.0020 (2)	−0.0505 (1)	0.6839 (2)	3.02 (4)
C(6)	0.7857 (2)	0.0416 (1)	0.6236 (2)	2.96 (4)
C(7)	0.7475 (2)	0.1124 (1)	0.5660 (2)	3.57 (5)
C(8)	0.6120 (3)	0.1422 (1)	0.5516 (2)	4.46 (6)
C(9)	0.5144 (2)	0.1009 (2)	0.5922 (2)	5.12 (6)
C(10)	0.5582 (2)	0.0315 (2)	0.6449 (2)	4.62 (5)
C(11)	0.7100 (3)	−0.0451 (2)	0.9596 (2)	5.52 (6)
C(12)	0.6813 (4)	−0.0446 (2)	1.0582 (3)	6.69 (8)
C(13)	0.6087 (4)	−0.1085 (2)	1.0851 (2)	6.68 (8)
C(14)	0.5630 (3)	−0.1672 (2)	1.0104 (2)	5.18 (6)
C(15)	0.5940 (2)	−0.1634 (1)	0.9083 (2)	3.48 (4)
C(16)	0.5745 (2)	−0.2507 (1)	0.7408 (2)	3.18 (4)
C(17)	0.5093 (2)	−0.3208 (1)	0.6932 (2)	4.12 (5)
C(18)	0.5485 (3)	−0.3530 (2)	0.6068 (2)	5.13 (6)
C(19)	0.6509 (3)	−0.3158 (2)	0.5673 (2)	4.88 (6)
C(20)	0.7034 (2)	−0.2453 (2)	0.6134 (2)	4.38 (5)
H(1)	0.990 (2)	−0.203 (2)	0.814 (2)	5.9*
H(2)	1.210 (2)	−0.231 (2)	0.796 (2)	6.4*
H(3)	1.314 (2)	−0.127 (2)	0.701 (2)	5.7*
H(4)	1.177 (2)	−0.019 (1)	0.634 (2)	4.7*
H(7)	0.818 (2)	0.141 (1)	0.537 (2)	4.7*
H(8)	0.587 (2)	0.193 (1)	0.516 (2)	5.8*
H(9)	0.429 (3)	0.119 (2)	0.583 (2)	6.6*
H(10)	0.498 (2)	0.001 (2)	0.678 (2)	6.0*
H(11)	0.762 (3)	−0.004 (2)	0.938 (2)	7.2*
H(12)	0.711 (3)	−0.001 (2)	1.105 (2)	8.7*
H(13)	0.593 (3)	−0.114 (2)	1.147 (3)	8.7*
H(14)	0.516 (3)	−0.210 (2)	1.019 (2)	6.7*
H(17)	0.444 (3)	−0.341 (2)	0.720 (2)	5.3*
H(18)	0.503 (3)	−0.400 (2)	0.576 (2)	6.6*
H(19)	0.680 (3)	−0.336 (2)	0.512 (2)	6.3*
H(20)	0.769 (2)	−0.216 (2)	0.590 (2)	5.7*
H(21)	0.969 (2)	0.045 (1)	0.617 (2)	4.3*
H(22)	0.487 (2)	−0.260 (1)	0.859 (2)	4.6*

* Atoms refined with fixed isotropic thermal parameters.

Fig. 1. *ORTEP* drawing with 30% thermal ellipsoids of the bis(di-2-pyridylamine)copper(I) cation.

Table 2. *Selected bond distances* (Å) *and angles* (°)

Cu—N(1)	2.022 (2)		C(1)—C(2)	1.359 (4)
Cu—N(3)	2.003 (2)		C(2)—C(3)	1.380 (4)
Cu—N(4)	2.019 (2)		C(3)—C(4)	1.364 (3)
Cu—N(6)	2.022 (2)		C(4)—C(5)	1.403 (3)
Cl—N(2)	3.221 (2)		C(6)—C(7)	1.392 (3)
N(1)—C(1)	1.351 (3)		C(7)—C(8)	1.369 (3)
N(1)—C(5)	1.334 (3)		C(8)—C(9)	1.379 (4)
N(2)—C(5)	1.376 (2)		C(9)—C(10)	1.355 (4)
N(2)—C(6)	1.381 (2)		C(11)—C(12)	1.347 (5)
N(3)—C(6)	1.340 (3)		C(12)—C(13)	1.377 (5)
N(3)—C(10)	1.356 (3)		C(13)—C(14)	1.354 (4)
N(4)—C(11)	1.352 (3)		C(14)—C(15)	1.402 (4)
N(4)—C(15)	1.336 (3)		C(16)—C(17)	1.394 (3)
N(5)—C(15)	1.376 (3)		C(17)—C(18)	1.361 (4)
N(5)—C(16)	1.385 (3)		C(18)—C(19)	1.376 (4)
N(6)—C(16)	1.338 (3)		C(19)—C(20)	1.358 (4)
N(6)—C(20)	1.351 (3)			
N(2)—H(21)	0.75 (3)		N(5)—H(22)	0.92 (3)
Cl···H(21)	2.48 (2)		Cl—H(22)	2.27 (2)
N(1)—Cu—N(3)	95.02 (7)		C(3)—C(4)—C(5)	119.2 (2)
N(1)—Cu—N(4)	128.29 (7)		N(1)—C(5)—N(2)	121.2 (2)
N(1)—Cu—N(6)	103.40 (7)		N(1)—C(5)—C(4)	121.9 (2)
N(3)—Cu—N(4)	112.50 (7)		N(2)—C(5)—C(4)	116.9 (2)
N(3)—Cu—N(6)	127.23 (6)		N(2)—C(6)—N(3)	121.4 (2)
N(4)—Cu—N(6)	93.71 (7)		N(2)—C(6)—C(7)	116.8 (2)
Cu—N(1)—C(1)	119.1 (2)		N(3)—C(6)—C(7)	121.8 (2)
Cu—N(1)—C(5)	123.3 (1)		C(6)—C(7)—C(8)	119.4 (2)
C(1)—N(1)—C(5)	116.9 (2)		C(7)—C(8)—C(9)	119.5 (2)
Cl···N(2)—C(5)	110.2 (1)		C(8)—C(9)—C(10)	117.7 (2)
Cl···N(2)—C(6)	114.3 (1)		N(3)—C(10)—C(9)	124.8 (2)
C(5)—N(2)—C(6)	135.1 (2)		N(4)—C(11)—C(12)	124.6 (3)
Cu—N(3)—C(6)	123.5 (1)		C(11)—C(12)—C(13)	118.0 (3)
Cu—N(3)—C(10)	119.7 (2)		C(12)—C(13)—C(14)	119.4 (3)
C(6)—N(3)—C(10)	116.7 (2)		C(13)—C(14)—C(15)	119.7 (3)
Cu—N(4)—C(11)	119.3 (2)		N(4)—C(15)—N(5)	121.7 (2)
Cu—N(4)—C(15)	123.4 (2)		N(4)—C(15)—C(14)	121.2 (2)
C(11)—N(4)—C(15)	117.0 (2)		N(5)—C(15)—C(14)	117.1 (2)
C(15)—N(5)—C(16)	133.6 (2)		N(5)—C(16)—N(6)	120.7 (2)
Cu—N(6)—C(16)	123.9 (1)		N(5)—C(16)—C(17)	117.7 (2)
Cu—N(6)—C(20)	119.0 (2)		N(6)—C(16)—C(17)	121.7 (2)
C(16)—N(6)—C(20)	116.9 (2)		C(16)—C(17)—C(18)	119.3 (2)
N(1)—C(1)—C(2)	124.6 (2)		C(17)—C(18)—C(19)	119.7 (2)
C(1)—C(2)—C(3)	117.9 (2)		C(18)—C(19)—C(20)	117.7 (2)
C(2)—C(3)—C(4)	119.5 (2)		N(6)—C(20)—C(19)	124.4 (2)
Cl···H(21)—N(2)	171 (2)		Cl···H(22)—N(5)	177 (2)

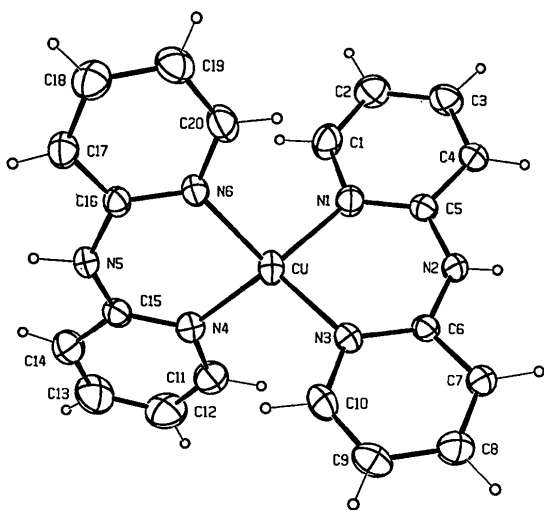Numbers in parentheses are e.s.d.'s in the least significant digits.

The dihedral angle between the pyridyl rings in di-2-pyridylamine varies widely depending on coordination of the ligand. This distortion of the molecule is also observed in the structure of free di-2-pyridylamine, where significant hydrogen bonding exists between the amine H atoms and the pyridyl N atom on two di-2-pyridylamines. The dihedral angle between the pyridyl groups is 23° (Johnson & Jacobson, 1973b). In four-coordinate [Cu^{II}(dpaH)$_2$]-(ClO$_4$)$_2$ (Johnson, Beineke & Jacobson, 1971), the two ligands are related by symmetry. No hydrogen bonding is evident, and the dihedral angle between the pyridyl rings is 9.6°.

In the present case the distortion in the ligand is also influenced by the hydrogen bonding from the amine H atom to the Cl counterions. The amine H atom on the di-2-pyridylamine ligand is known to beome more acidic upon complexation due to polarization of the ligand electron density by the positively charged metal ion. The N—H bond lengths are 0.75 (3) and 0.92 (3) Å, and the respective Cl···H distances are 2.48 (2) and 2.27 (2) Å. The

bond angles for the N—H⋯Cl hydrogen bond are 171 (2) and 177 (2)°, respectively. Both bonds are close to the expected 180° for hydrogen bonding of this type. The amine H atom that exhibits the more linear and shorter hydrogen bond is on the ligand which is more distorted from planarity, suggesting that this may be the origin of the distortion.

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Structure of [PhCH2NMe3]2[(B10H12)2Pd] Acetonitrile Solvate

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Abstract. $[PhCH_2NMe_3]_2^+ \cdot [Pd(B_{10}H_{12})_2]^{2-} \cdot 2CH_3CN$, $M_r = 729 \cdot 39$, triclinic, $P\bar{1}$, $a = 9 \cdot 2094$ (18), $b = 10 \cdot 772$ (3), $c = 11 \cdot 3707$ (23) Å, $\alpha = 67 \cdot 721$ (21), $\beta = 83 \cdot 394$ (16), $\gamma = 78 \cdot 801$ (21)°, $V = 1022 \cdot 8$ Å^3, $Z = 1$, $D_x = 1 \cdot 184$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 0 \cdot 470$ mm^{-1}, $F(000) = 380$, $T = 291$ (1) K, $R = 0 \cdot 0265$ for 5850 independent observed reflections. The palladaborane anion has effective C_{2h} molecular symmetry (C_i imposed). The $\{B_{10}\}$ fragment has a geometry close to intermediate between that of *nido*-$\{B_{10}H_{12}\}^{2-}$ and *arachno*-$\{B_{10}H_{12}\}^{4-}$, and the verticity of the Pd atom is 39·4%.

Introduction. We are involved in a major research programme which critically examines the structures of metallaboranes and metallaheteroboranes. The aims of the work are firstly to measure the extent to which the metal atom present can be regarded as a true cluster vertex, and then to determine the factors responsible for the 'verticity' of the metal. The family of metallaboranes represented by $MB_{10}H_{12}$ is particularly useful in this respect, since the $\{B_{10}H_{12}\}$ ligand appears able to accommodate both metal vertices and (non-vertex) metal bridges with only subtle, but nevertheless measureable, structural change. In brief, if the metal is formally present as a polyhedral vertex the $\{B_{10}H_{12}\}$ ligand is formally the *arachno* fragment $\{B_{10}H_{12}\}^{4-}$, whereas for a bridging metal atom the polyhedral unit is merely the *nido* species $\{B_{10}H_{12}\}^{2-}$.

We have previously shown that clear examples of both types of metallaborane exist. Thus, in [7,7,7-(CO)$_3$-*nido*-7-CoB$_{10}$H$_{12}$]$^-$ (Macgregor, Yellowlees & Welch, 1990a) the Co atom, formally Co^{3+}, is a true polyhedral vertex (high verticity), whereas in (the superficially structurally similar) [5,6,9,10-μ_4-{AuP(C$_6$H$_{11}$)$_3$}-*nido*-B$_{10}$H$_{12}$]$^-$ (Wynd, Welch & Parish, 1990), the Au atom, formally Au$^+$, is not (low verticity).

We recently showed (Macgregor, Yellowlees & Welch, 1990b) that metallaboranes of the type $[(B_{10}H_{12})_2M]^{n-}$ [M = Ni, $n = 2$ (Guggenberger, 1972); M = Pt, $n = 2$ (Macgregor, Yellowlees & Welch, 1990b); M = Au, $n = 1$ (Wynd & Welch, 1987)] are particularly interesting in that they show intermediate behaviour, *i.e.* the $\{B_{10}H_{12}\}$ fragments of the molecules have structures that lie between those expected for $\{B_{10}H_{12}\}^{2-}$ and $\{B_{10}H_{12}\}^{4-}$, resulting in metal verticities that are neither high nor low. The situation was further complicated by the fact that the platinaborane structure appeared to suffer from an unusual asymmetry which we were forced to conclude was the result of crystal packing effects. Seeking further data on the $[(B_{10}H_{12})_2M]^{n-}$