Metal Complexes of Multidentate Ligands containing Carbonyl and α-Di-imine groups. Crystal and Molecular Structure of Aquabis[2-(2-pyridyl)quinazolin-4(3*H*)-onato]copper(II)

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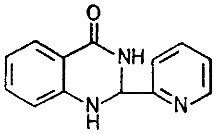
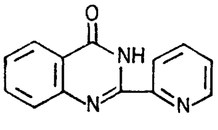
The title compound (IV) has been prepared and its structure determined from X-ray diffraction data. The structure was solved by Patterson and Fourier methods and refined using least-squares techniques to R 4.1% for 3 258 independent reflections. Crystals are triclinic, space group $P\bar{1}$ with unit cell dimensions $a = 12.20(1)$, $b = 13.91(1)$, $c = 7.35(1)$ Å; $\alpha = 91.7(1)$, $\beta = 112.7(1)$, $\gamma = 103.9(1)°$, $Z = 2$. Co-ordination round copper is approximately square pyramidal: a water molecule [Cu–O 2.014(4) Å], a chelate ligand [Cu–N(py) 2.022(4), Cu–N 1.992(4) Å], and one nitrogen atom [Cu–N 1·967(4) Å] of the second chelate ligand form the base, and the pyridine nitrogen [Cu–N(py) 2.245(4) Å] of the second ligand forms the apex.

DURING recent investigations [1-4] of copper(II) complexes of organic ligands containing the C=O group and the N–C–C–N system, the ligand behaviour of (I) 2-(2-pyridyl)-2,3-dihydroquinazolin-4(1*H*)-one was considered.



(I) (Ligand HL)



(II) (Ligand HL′)

A mixed-chelated nickel(II) complex [5] with it was examined by X-ray diffraction and i.r. spectroscopy. We have now isolated a copper(II) complex obtained from the reaction of this same ligand with copper(II) chloride in acetone solution. We now report its spectroscopic properties and X-ray analysis, and show that the parent ligand has become oxidized to (II), 2-(2-pyridyl)-quinazolin-4(3*H*)-one.

EXPERIMENTAL

Preparation of (I) 2-(2-*pyridyl*)-2,3-*dihydroquinazolin*-4-(1*H*)-*one*.—*o*-Aminobenzamide and pyridine-2-carbaldehyde (molar ratio 1 : 1) were heated under reflux for 3—4 h in benzene solution. By slow evaporation of the solvent, a cream-coloured microcrystalline product was isolated, m.p. 185 °C (Found: C, 69.2; H, 5.4; N, 18.8. Calc. for $C_{13}H_{11}N_3O$: C, 69.3; H, 5.35; N, 18.65%).

Preparation of the Copper(II) *Complex*.—$CuCl_2·2H_2O$ and (I) (molar ratio 1 : 1) were heated under reflux in acetone solution for 1 h. After some hours at room temperature, a green crystalline product of formula $Cu(C_{13}H_8N_3O)Cl·H_2O$ was obtained (Found: C, 46.25; H, 3.1; Cu, 19.0; N, 12.5. Calc.: C, 46.0; H, 3.0; Cu, 18.7; N, 12.4%). By successive recrystallization of this compound from boiling dimethyl sulphoxide, green prisms of formula $Cu(C_{13}H_8N_3O)_2·H_2O$ were obtained (Found: C, 58.6; H, 3.6; Cu, 11.75; N, 15.8. Calc.: C, 59.4; H, 3.45; Cu, 12.1; N, 16.0%).

I.r. and electronic spectra were recorded on Perkin-Elmer 457 and 402 spectrophotometers respectively. X-Ray intensity data were collected on a Siemens AED single-crystal computer-controlled diffractometer.

Crystal Data.—$C_{26}H_{18}CuN_6O_3$, $M = 526$, Triclinic, $a = 12.20(1)$, $b = 13.91(1)$, $c = 7.35(1)$ Å, $\alpha = 91.7(1)$, $\beta = 112.7(1)$, $\gamma = 103.9(1)°$, $U = 1\,112$ Å^3, $D_m = 1.59$ g cm^{-3}, $Z = 2$, $D_c = 1.57$ g cm^{-3}, $F(000) = 546$. Cu-K_α radiation $\lambda = 1.5418$ Å, $\mu(\text{Cu-}K_\alpha) = 17.9$ cm^{-1}. Space group $P\bar{1}$ from structural analysis.

Cell dimensions were determined from rotation and Weissenberg photographs and refined from diffractometer measurements.

Intensity Data Collection.—A sample was aligned with its [001] axis along the ϕ axis of the diffractometer and all reflections with $6° \leqslant 2\theta \leqslant 120°$ were collected. In this way the intensities of 3 258 independent reflections were measured, and 2 878 of them, having $I > 2\sigma(I)$, were considered observed and were used in the structure analysis.

There was no evidence for decomposition of the sample during the X-ray exposure as shown by the constant intensity of a standard reflection measured every 20 reflections.

After the usual data reduction structure amplitudes were put on an absolute scale first by Wilson's method,[6] then by comparison with the calculated values. Absorption corrections were not applied, in view of the low absorbance of the sample ($\mu\bar{r}$ 0.13).

Structure Determination and Refinement.—The structure was solved by the heavy-atom technique, taking copper co-ordinates obtained from a three-dimensional Patterson calculation. Refinement by block-diagonal anisotropic least-squares gave R 5.6%. The function minimized was $\Sigma w|\Delta F|^2$, first with unit weights, then with the weighting scheme $w = 1/(A + BF_o)^2$, where $A = 2.40$ and $B = 0.02$. In the last stages of the refinement the hydrogen atoms, which had been located from a difference-Fourier map, were included and refined isotropically, to give a final R of 4.1%.

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[1] A. Mangia, M. Nardelli, C. Pelizzi, and G. Pelizzi, *Acta Cryst.*, 1974, **B30**, 17.

[2] A. Mangia, C. Pelizzi, and G. Pelizzi, *Acta Cryst.*, 1974, **B30**, 2146.

[3] P. Domiano, A. Musatti, M. Nardelli, C. Pelizzi, and G. Predieri, *J.C.S. Dalton*, 1975, 2357.

[4] C. Pelizzi and G. Predieri, *Gazzetta*, 1975, **105**, 413.

[5] A. Bonamartini Corradi, C. Grasselli Palmieri, M. Nardelli, and C. Pelizzi, *J.C.S. Dalton*, 1974, 150.

[6] A. J. C. Wilson, *Nature*, 1942, **150**, 151.

Final positional parameters with their standard deviations are given in Tables 1 and 2. Observed and calculated structure factors with thermal parameters and individual bond lengths and angles in the organic ligands are listed in Supplementary Publication No. SUP 21636 (17 pp., 1 microfiche).* Atomic scattering factors used throughout the calculations were taken from ref. 7 for non-hydrogen atoms and for hydrogen atoms from ref. 8.

TABLE 1

Final atomic fractional co-ordinates (× 10^4) with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*
Cu	2 337(1)	2 233(1)	2 694(1)
O(1)	257(2)	3 109(2)	505(4)
O(2)	4 663(3)	2 201(2)	1 524(5)
O(3)	2 299(2)	1 805(2)	23(4)
N(1)	2 146(2)	701(2)	3 628(4)
N(2)	538(2)	1 671(2)	1 715(4)
N(3)	−1 126(2)	260(2)	1 332(4)
N(4)	2 451(3)	3 057(2)	5 106(4)
N(5)	4 133(2)	2 932(2)	3 762(5)
N(6)	5 642(3)	4 168(2)	6 439(5)
C(1)	962(3)	182(2)	3 063(5)
C(2)	621(3)	−779(3)	3 496(5)
C(3)	1 536(4)	−1 220(3)	4 514(6)
C(4)	2 753(4)	−703(3)	5 094(6)
C(5)	3 017(3)	256(3)	4 606(6)
C(6)	47(3)	725(2)	1 957(5)
C(7)	−198(3)	2 256(3)	747(5)
C(8)	−1 525(3)	1 805(3)	86(5)
C(9)	−1 933(3)	817(3)	417(5)
C(10)	−3 209(3)	383(3)	−189(5)
C(11)	−4 019(3)	929(3)	−1 073(6)
C(12)	−3 604(4)	1 915(3)	−1 419(6)
C(13)	−2 368(4)	2 345(3)	−847(6)
C(14)	1 553(3)	3 053(3)	5 742(6)
C(15)	1 736(4)	3 627(3)	7 428(6)
C(16)	2 883(5)	4 266(4)	8 494(7)
C(17)	3 813(4)	4 280(4)	7 828(7)
C(18)	3 573(3)	3 654(3)	6 172(5)
C(19)	4 537(3)	3 602(3)	5 426(5)
C(20)	4 973(3)	2 790(3)	3 032(6)
C(21)	6 247(3)	3 393(3)	4 111(6)
C(22)	6 523(3)	4 064(3)	5 748(6)
C(23)	7 749(4)	4 671(3)	6 780(7)
C(24)	8 637(4)	4 555(3)	6 125(8)
C(25)	8 358(4)	3 872(3)	4 496(8)
C(26)	7 165(4)	3 285(3)	3 460(7)

TABLE 2

Final fractional co-ordinates (× 10^3) and isotropic thermal parameter (× 10^2 Å^2) of hydrogen atoms, with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*	*B*
HC(2)	−22(3)	−111(3)	316(5)	42(8)
HC(3)	133(3)	−190(3)	481(5)	49(9)
HC(4)	331(4)	−100(3)	547(6)	53(9)
HC(5)	386(3)	67(3)	495(5)	49(9)
HC(10)	−349(3)	−32(3)	3(5)	40(8)
HC(11)	−489(3)	63(3)	−143(5)	46(9)
HC(12)	−418(4)	230(3)	−200(6)	56(10)
HC(13)	−203(3)	299(3)	−113(6)	52(9)
HC(14)	74(3)	262(3)	491(5)	45(9)
HC(15)	105(4)	359(3)	786(6)	57(10)
HC(16)	304(4)	473(3)	974(7)	73(12)
HC(17)	462(4)	472(3)	849(6)	70(11)
HC(23)	797(3)	518(3)	799(5)	46(9)
HC(24)	950(4)	496(3)	690(6)	66(11)
HC(25)	900(4)	380(3)	404(6)	68(11)
HC(26)	696(4)	280(3)	225(6)	68(11)
H(1)O(3)	189(4)	117(3)	−56(6)	57(10)
H(2)O(3)	308(4)	190(3)	28(6)	58(10)

All calculations were performed on a CDC 6600 computer at the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale with programs of Immirzi.[9]

RESULTS AND DISCUSSION

I.r. Spectra.—Table 3 lists the main vibrational bands with their assignments for the organic ligand (I), and of the two copper complexes (III) and (IV). The spectra of the two complexes are characterized by the disappearance of the vibrational modes due to the N–H groups and by the presence of the absorptions bands of C=O, C=N, and aromatic rings. In particular, the band at *ca.* 1 540 cm^{-1} is likely to be due to the stretching vibration of the imine C=N group. The band at 1 663 cm^{-1} in the spectrum of (I) was assigned to ν(CO); the occurrence of such a band in the complexes (1 630 cm^{-1}) at lower frequencies is a consequence of the deprotonation of the CONH system. Several pyridine bands are shifted towards higher frequencies in the region 1 600—1 400 cm^{-1}, indicating that the nitrogen atom is involved in co-ordination.

TABLE 3

Main vibrational bands (cm^{-1}) for (I), $CuL'Cl\cdot H_2O$ (III), and $CuL'_2\cdot H_2O$ (IV).

(I)	(III)	(IV)	Assignment
3 290ms			ν(N–H)
3 180m			ν(N–H)
3 060m	3 100m	3 060m	ν(C–H)
2 920m	3 050m	3 040sh	ν(C–H)
1 663vs	1 630sh	1 630vs	ν(C=O)
1 610s			δ(N–H)
1 590m	1 605sh	1 605s	py
1 570m	1 580s	1 585s	py
	1 560m	1 570sh	py
	1 535s	1 545sh	ν(C=N)
		1 530vs	
1 510ms			ν(C–N)
1 485m	1 475sh	1 485sh	py
1 470m	1 468vs	1 473s	py
1 450m	1 445m	1 450m	py

m = medium, ms = medium strong, sh = shoulder, s = strong, vs = very strong.

Electronic Spectra.—The electronic absorption spectra of the two copper(II) complexes have been measured in dimethyl sulphoxide solution and in the solid state by diffuse reflectance. In the u.v. region, both compounds show a strong band at 325 nm, with shoulders at 280 and 340 nm, which can be attributed to electronic transitions in the ligand (a probable metal–ligand charge-transfer is present in the 340 nm shoulder). The spectrum of $CuL'Cl\cdot H_2O$ (III) dissolved in dimethyl sulphoxide shows a broad band at 740 nm (at 700 nm in diffuse reflectance spectrum) indicating probable five-co-ordination.[10] The band at 750 nm in the solid-state spectrum of (IV), which is in agreement with five-co-ordination for copper, disappears when the complex is dissolved in dimethyl sulphoxide, to be replaced by a broad band at 630 nm,

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

[7] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[9] A. Immirzi, *Ricerca Sci.*, 1967, **34**, 743.

[10] B. J. Hathaway, *J.C.S. Dalton*, 1972, 1196.

TABLE 4

Bond distances (Å) and angles (°) with their estimated standard deviations in parentheses

(*a*) In the co-ordination polyhedron

Cu–N(1)	2.245(4)	N(1)–Cu–N(2)	76.9(2)	N(2)–Cu–N(5)	174.2(3.1)
Cu–N(2)	1.967(4)	N(1)–Cu–N(4)	101.6(3)	N(2)–Cu–O(3)	91.1(3)
Cu–N(4)	2.022(4)	N(1)–Cu–N(5)	107.6(3)	N(4)–Cu–N(5)	82.1(3)
Cu–N(5)	1.992(4)	N(1)–Cu–O(3)	95.1(3)	N(4)–Cu–O(3)	163.3(1.8)
Cu–O(3)	2.014(4)	N(2)–Cu–N(4)	93.5(3)	N(5)–Cu–O(3)	92.2(3)

(*b*) In the organic ligands (means for two independent molecules)

N(4)–C(14), N(1)–C(5)	1.340(4)	C(4)–C(5), C(14)–C(15)	1.378(4)
C(3)–C(4), C(15)–C(16)	1.372(4)	C(2)–C(3), C(16)–C(17)	1.382(5)
C(1)–C(2), C(17)–C(18)	1.379(4)	N(4)–C(18), N(1)–C(1)	1.335(3)
C(1)–C(6), C(18)–C(19)	1.491(4)	N(2)–C(6), N(5)–C(19)	1.358(3)
N(2)–C(7), N(5)–C(20)	1.370(4)	O(1)–C(7), O(2)–C(20)	1.233(4)
C(7)–C(8), C(20)–C(21)	1.461(4)	N(3)–C(9), N(6)–C(22)	1.384(4)
N(3)–C(6), N(6)–C(19)	1.302(3)	C(8)–C(9), C(21)–C(22)	1.393(4)

(C–C) (benzene ring) 1.394(2)

C(1)–N(1)–C(5), C(14)–N(4)–C(18)	118.1(6)	N(1)–C(5)–C(4), N(4)–C(14)–C(15)	123.4(6)
N(1)–C(1)–C(2), N(4)–C(18)–C(17)	122.2(5)	C(1)–C(2)–C(3), C(18)–C(17)–C(16)	118.9(6)
C(2)–C(3)–C(4), C(17)–C(16)–C(15)	119.3(6)	C(3)–C(4)–C(5), C(16)–C(14)–C(15)	118.2(6)
N(4)–C(18)–C(19), N(1)–C(1)–C(6)	115.1(5)	C(17)–C(18)–C(19), C(2)–C(1)–C(6)	122.8(6)
N(5)–C(19)–C(8), N(2)–C(6)–C(1)	115.0(4)	N(6)–C(19)–C(18), N(3)–C(6)–C(1)	118.2(5)
O(1)–C(7)–C(8), C(20)–C(21)–O(2)	122.9(5)	O(1)–C(7)–N(2), O(2)–C(20)–N(5)	120.3(6)
N(2)–C(6)–N(3), N(5)–C(19)–N(6)	127.4(5)	C(6)–N(2)–C(7), C(19)–N(5)–C(20)	120.3(5)
N(2)–C(7)–C(8), N(5)–C(20)–C(21)	116.0(4)	C(7)–C(8)–C(9), C(20)–C(21)–C(22)	118.7(5)
C(7)–C(8)–C(13), C(20)–C(21)–C(26)	120.3(6)	C(8)–C(9)–N(3), C(21)–C(22)–N(6)	122.3(6)
N(3)–C(9)–C(10), N(6)–C(22)–C(23)	119.7(5)	C(9)–N(3)–C(6), C(22)–N(6)–C(19)	115.5(5)

(C–C–C) (benzene ring) 119.9(2)

(*c*) Bond distances involving the hydrogen atoms are in the range 0.84—1.03 Å; those involving the water molecules are 0.87 and 0.90 Å

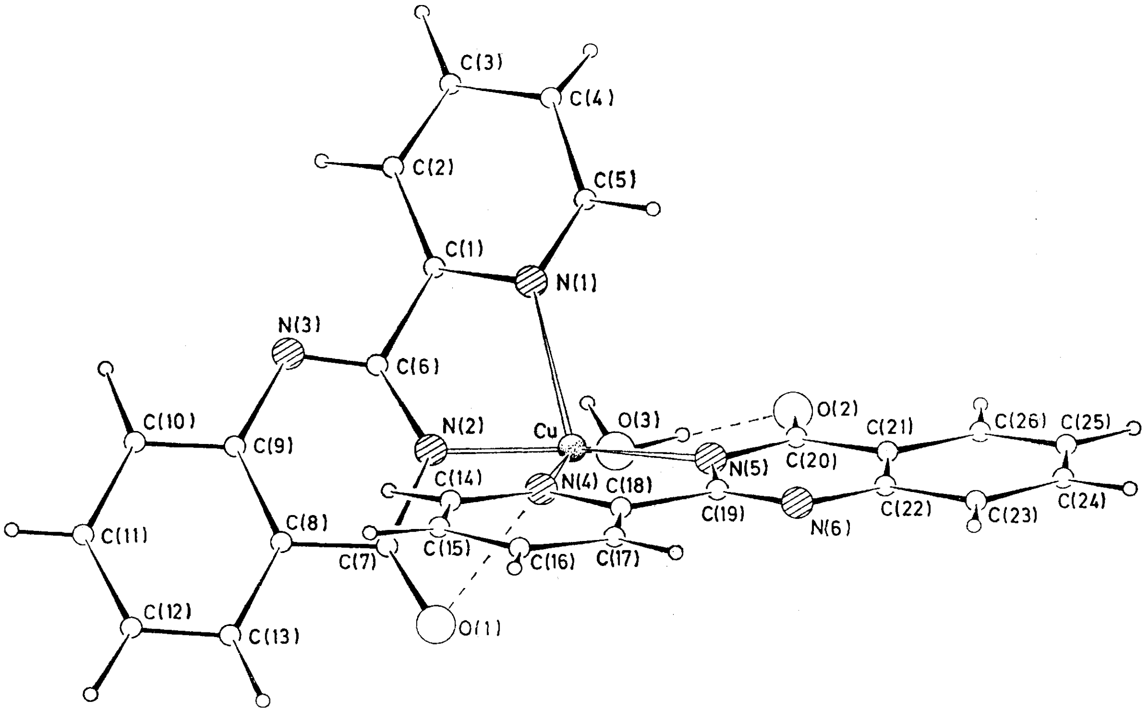

FIGURE 1 Clinographic projection of the complex molecule

indicating that the co-ordination has changed, probably to octahedral.

X-Ray Structure.—In agreement with the disappearance of the N–H vibrational bands in the i.r. spectrum, the *X*-ray analysis confirms the deprotonation of the original ligand (I) and its oxidation, which produced a C=N double bond nearly localized between C(6)–N(3) 1.31 and C(19)–N(6) 1.29 Å (theoretical 1.265 Å).[11] Co-ordination of copper involves two organic molecules, which act as bidentate ligands through the pyridine nitrogen and the quinazoline nitrogen adjacent to the C=O group, to form two five-membered chelate rings (Figure 1). In this way, the co-ordination polyhedron results in a distorted square pyramid involving four

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[11] J. Donohue, L. R. Lavine, and J. S. Rollett, *Acta Cryst.*, 1956, **9**, 655.

nitrogen atoms and the oxygen atom of the water molecule. The water molecule is not situated at the apex of the pyramid, as is frequently found in five-co-ordinate copper(II) complexes,[12,13] but it is at the base of the pyramid. This unusual behaviour can be explained by the rather strong intermolecular hydrogen bonding (2.566 Å) formed by the water molecule with a C=O group of an adjacent ligand.

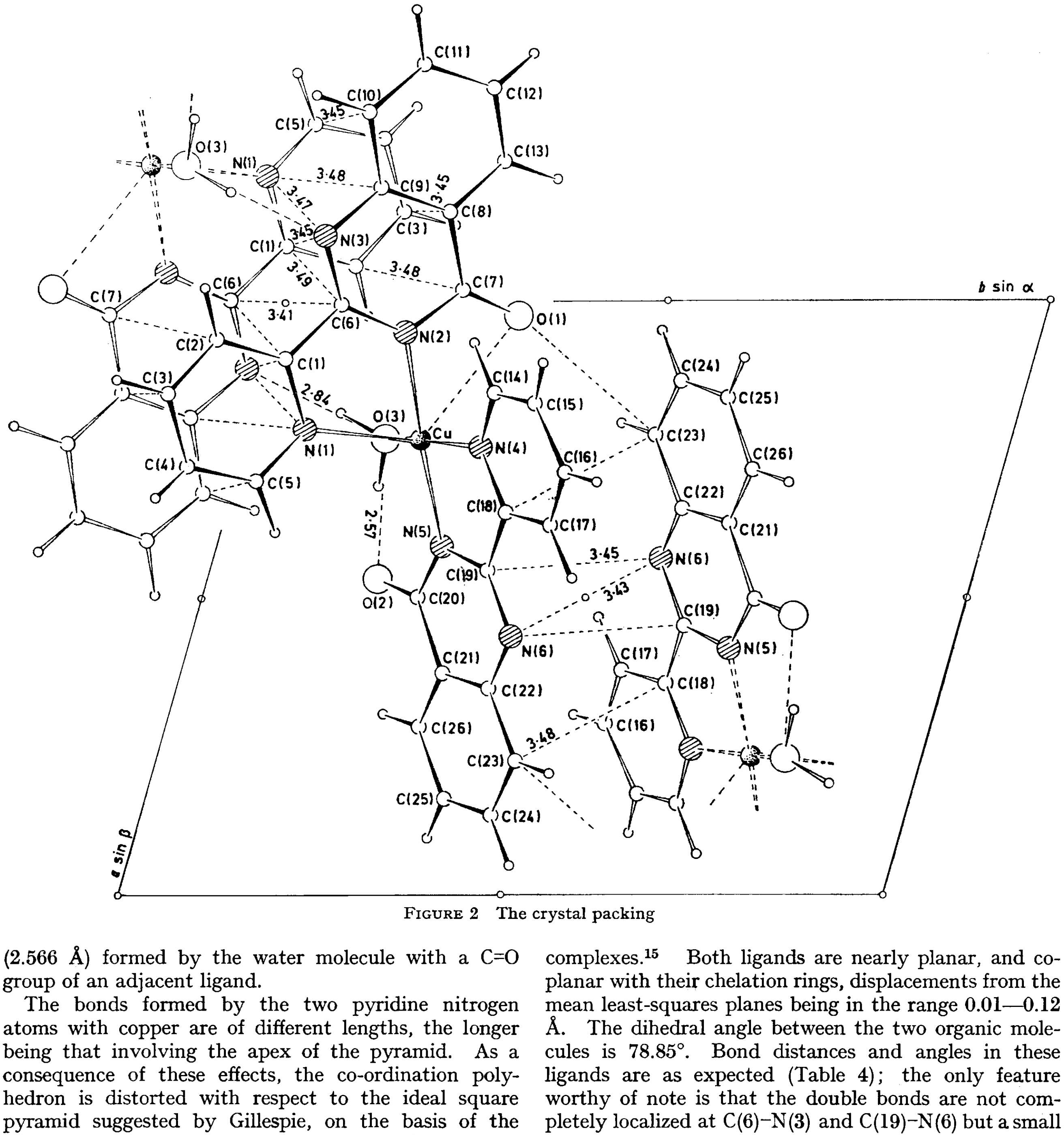

Figure 2 The crystal packing

The bonds formed by the two pyridine nitrogen atoms with copper are of different lengths, the longer being that involving the apex of the pyramid. As a consequence of these effects, the co-ordination polyhedron is distorted with respect to the ideal square pyramid suggested by Gillespie, on the basis of the valence-shell electron-pair repulsion theory.[14] The copper atom is out of the basal plane N(2),N(4),N(5),O(3) by 0.17 Å.

A sixth co-ordination site, severely distorted from octahedral, is occupied by a carbonyl oxygen atom which is 2.994 Å away from copper. This 5 + 1 distorted arrangement has been observed in many copper(II) complexes.[15] Both ligands are nearly planar, and coplanar with their chelation rings, displacements from the mean least-squares planes being in the range 0.01—0.12 Å. The dihedral angle between the two organic molecules is 78.85°. Bond distances and angles in these ligands are as expected (Table 4); the only feature worthy of note is that the double bonds are not completely localized at C(6)–N(3) and C(19)–N(6) but a small π-delocalization is extended onto the adjacent N(3)–C(9), C(6)–N(2), and N(6)–C(22), C(19)–N(5) bonds shown

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[12] A. Mangia, M. Nardelli, C. Pelizzi, and G. Pelizzi, *J.C.S. Dalton*, 1972, 2483.

[13] T. S. Cameron, K. Prout, F. J. C. Rossotti, and D. Steele, *J.C.S. Dalton*, 1973, 2626.

[14] R. J. Gillespie, *J. Chem. Soc.*, 1963, 4670, 4672.

[15] B. F. Hoskins and F. D. Whilliams, *Co-ordination Chem. Rev.*, 1972, **9**, 365.

by their lengths, which are a little shorter than the theoretical value (1.44 Å) for a C(sp^2)–N(sp^2) single bond. Some π-delocalization is also present along the O(1),C(7),-N(2) and O(2),C(20),N(5) amide groups.

Comparison of the conformation of the organic ligand (II) in the copper complex with that of (I) in the nickel complex[5] shows that the pyridine group assumes different orientations in the two complexes, in order to allow bidentate chelation in each.

The water molecule forms two hydrogen bonds: one intramolecular [O(3)–H $\cdots$ O(2) 2.566 Å] which is rather short, the other intermolecular [O(3)–H $\cdots$ N(3^{I}) 2.837 Å] which is normal. The complex molecule is packed in the crystal in such a way that the organic ligands are facing their analogues in adjacent molecules through the centre of symmetry at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, thus forming ribbons along [111] (Figure 2). The other contacts <3.50 Å are: O(3) $\cdots$ C(2^{I}) 3.412(7), O(3) $\cdots$ C(10^{II}) 3.472(6), O(1) $\cdots$ C(15^{II}) 3.393(7), and O(3) $\cdots$ C(15^{II}) 3.263(6), where superscripts refer to the equivalent positions I at $\bar{x}, \bar{y}, \bar{z}$, and II at $x, y, z - 1$.

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