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Studies on the Metal–Amide Bond. XIII*. The Crystal and Molecular Structure of the β-Form of Aqua[N,N′-bis(2′-pyridinecarboxamido)-1,3-propane]copper(II) Dihydrate

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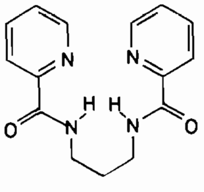
β-Aqua [N,N′-bis(2′-pyridinecarboxamido)1,3-propane]δ-copper(II) dihydrate, $C_{15}H_{20}N_4O_5Cu$, *is monoclinic, space group* $P2_1/n$, *with* a = *6.939(9),* b = *12.615(16),* c = *19.472(20) Å, β = 97.15(8)°,* Z = *4. The structure was refined to* R = *0.086 for 2492 photographic reflexions by full-matrix least-squares procedures. The Cu atom geometry is a distorted square-based pyramid, with the ligand encompassing the base [average Cu–Nδ-(amide) 1.954(5) Å, average Cu–N(*pyridine*) 2.065(5) Å, N(*amide*)–Cu–N(*amide*) 93.7(2)°, N(*pyridine*)–Cu–N(*pyridine*) 101.1(2)°], from which the Cu atom is displaced 0.24 Å towards an apical water molecule [Cu–O 2.268(4) Å]. A close contact between α-pyridyl H atoms (1.86 Å) causes folding of 26.2° between the two nearly planar picolinamide units, with the central six-membered chelate ring adopting a boat conformation. Enforced steric strain in the molecule results in non-planar distortions in the pyridine rings, although the coordinated amide groups remain planar. The coordinated and lattice water molecules are involved in a hydrogen-bonding network incorporating the amide oxygen atoms and giving rise to sheets perpendicular to* b.

Introduction

Each of the bis-picolinamide ligands investigated thus far in this series of papers has been observed to coordinate to a metal ion on deprotonation to generate a 5-,5-,5-membered system of chelate rings. Both X-ray diffraction [1–8] and NMR [9] techniques have indicated close contacts of the α-hydrogen atoms of the terminal pyridyl groups, often resulting in large distortions from planarity in the tetradentate ligands. This 'B strain' effect [10] would become more pronounced in analogous ligands which generate a 5-, 6-, 5-membered chelate ring system, due to the resulting closer approach of the pyridyl groups. The bis(amide) N,N′-bis(2′-pyridinecarboxamide)-1,3-propane (bppnH$_2$), *I*, [11] is one such ligand. A spectral investigation of its deprotonated Cu(II) and Ni(II) chelates had been reported earlier [12]. The ligand forms a wide variety of metal complexes [13] similar to its 1,2-ethane homologue, bpenH$_2$ [9]. At high pH two crystalline forms of the compound Cu(bppn)·3H$_2$O separate from aqueous solution. The initial product, designated the α-form, crystallises as deep–blue rhomboids of appearance similar to [Cu(bpen)H$_2$O]H$_2$O [2] and has not yet been structurally investigated. Upon prolonged standing long blue needles separate from the mother liquor. This paper describes the determination of the crystal structure of the latter product, designated the β-form.



(I)

bppnH$_2$

Experimental

The compound was obtained as deep–blue needles with [100] elongation.

Crystal Data

$C_{15}H_{20}N_4O_5Cu$, M_r = 400.1, Monoclinic, a = 6.939(9), b = 12.615(16), c = 19.472(20) Å, β = 97.15(8)°, U = 1691.2 Å^3, D_m = 1.55 (by flotation), Z = 4, D_c = 1.571 Mg m^{-3}, $F(000)$ = 828, μ(Cu-K_α) = 2.18 mm^{-1}. Systematic absences $0k0$ when $k \neq 2n$, $h0l$ when $h + l \neq 2n$, space group $P2_1/n$ (non-std., No. 14).

Unit cell parameters were determined from oscillation and Weissenberg photographs with Cu-K_α radiation. Using the Weissenberg equi-inclination

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*Part XII is reference [8].

TABLE I. Final Atomic Coordinates (fractional, $\times 10^4$) with Estimated Standard Deviations in Parentheses.

	x	y	z
Cu	2950.9(11)	645.8(5)	1489.5(3)
O(W1)	4467(7)	−531(3)	858(2)
O(W2)	1645(8)	378(4)	4232(2)
O(W3)	8143(8)	−811(4)	4334(2)
O(1)	4785(7)	−210(3)	3466(2)
O(2)	−2504(7)	664(3)	489(2)
N(1)	3121(7)	−108(3)	2370(2)
N(2)	257(7)	223(3)	1208(2)
N(11)	5430(7)	1360(3)	1990(2)
N(21)	2346(8)	1618(4)	644(2)
C(1)	1744(10)	−921(5)	2548(3)
C(2)	−731(9)	−668(4)	1491(3)
C(3)	688(9)	−1404(4)	1892(3)
C(01)	4526(9)	136(4)	2850(2)
C(02)	−724(9)	780(4)	724(3)
C(11)	5935(8)	921(4)	2615(2)
C(12)	7628(9)	1183(4)	3023(3)
C(13)	8854(12)	1933(6)	2785(4)
C(14)	8331(11)	2403(5)	2171(3)
C(15)	6621(10)	2098(4)	1783(3)
C(21)	405(9)	1626(4)	422(2)
C(22)	−403(10)	2323(5)	−71(3)
C(23)	812(12)	3027(5)	−306(3)
C(24)	2768(12)	2971(5)	−182(3)
C(25)	3504(11)	2244(5)	313(3)

TABLE II. Hydrogen Atomic Parameters (coordinates: fractional $\times 10^3$).[a]

	x	y	z
H(1a)	73	−70	271
H(1b)	228	−140	289
H(2a)	−173	−79	118
H(2b)	−120	−50	182
H(3a)	0	−210	200
H(3b)	139	−152	170
H(12)	800	82	349
H(13)	1011	213	307
H(14)	917	297	200
H(15)	623	245	132
H(22)	−187	232	−22
H(23)	23	360	−69
H(24)	373	343	−41
H(25)	494	216	44
H(W11)	546	−14	74
H(W12)	384	−57	42
H(W21)	262	19	399
H(W22)	54	4	414
H(W31)	706	−62	405
H(W32)	812	−71	480

[a] For all H atoms $B = 5.0$ Å^2.

TABLE III. Final Anisotropic Thermal Parameters ($\times 10^4$) in the Form $\exp -(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})$ with Estimated Standard Deviations in Parentheses.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cu	106(3)	37.8(6)	13.5(3)	−11.1(6)	−0.7(6)	4.3(2)
O(W1)	79(11)	65(3)	12(1)	−1(4)	2(3)	−1(1)
O(W2)	149(14)	82(4)	23(1)	−9(6)	19(4)	−9(2)
O(W3)	146(13)	63(3)	19(1)	10(5)	−4(3)	1(1)
O(1)	125(11)	49(3)	10(1)	−1(4)	3(2)	9(1)
O(2)	56(10)	71(3)	13(1)	−8(4)	−2(3)	5(1)
N(1)	70(12)	30(2)	12(1)	−16(4)	4(3)	7(1)
N(2)	109(12)	24(2)	9(1)	−14(4)	4(3)	0(1)
N(11)	107(12)	31(2)	9(1)	−4(4)	2(3)	1(1)
N(21)	118(13)	39(3)	12(1)	−17(4)	−8(3)	6(1)
C(1)	136(16)	43(3)	13(1)	−33(6)	9(4)	9(2)
C(2)	94(15)	38(3)	13(1)	−17(5)	4(4)	4(1)
C(3)	124(15)	22(3)	16(1)	−13(5)	5(4)	3(1)
C(01)	94(14)	28(3)	8(1)	6(5)	0(3)	2(1)
C(02)	71(14)	29(3)	10(1)	−2(4)	9(4)	−1(1)
C(11)	82(13)	22(2)	8(1)	−1(4)	4(3)	−2(1)
C(12)	84(14)	44(3)	15(1)	−10(5)	−2(4)	−1(2)
C(13)	161(20)	60(4)	21(2)	−25(7)	−6(5)	0(2)
C(14)	129(17)	59(4)	24(2)	−47(7)	6(5)	2(2)
C(15)	138(17)	43(4)	13(1)	−24(6)	11(4)	1(2)
C(21)	109(15)	32(3)	9(1)	−7(5)	3(4)	−1(1)
C(22)	124(16)	48(3)	12(1)	20(6)	6(4)	3(2)
C(23)	237(23)	36(4)	17(2)	−2(6)	−7(5)	9(2)
C(24)	207(22)	50(4)	18(2)	−35(7)	−18(5)	13(2)
C(25)	155(18)	60(4)	16(2)	−35(7)	−7(4)	12(2)

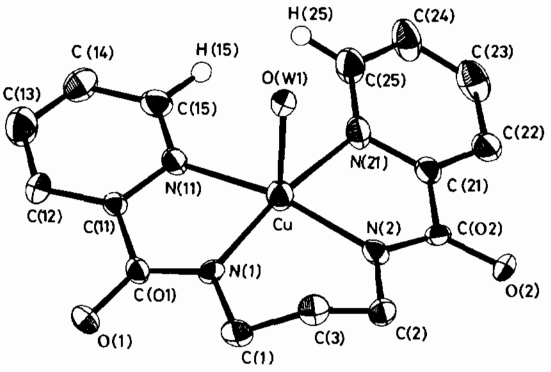

Fig. 1. A perspective drawing of the chelate molecule showing the atomic labelling. H atoms other than those in the 6′-positions of the pyridyl rings have been omitted for clarity. Thermal ellipsoids of non-hydrogen atoms are scaled to include 50% probability.

technique 2934 non-zero reflexions were recorded from layers 0–4*kl*, *h*0–3*l* and *hk*0–3. Their intensities were estimated visually and were corrected for Lorentz and polarization effects but not for absorption or extinction. The observed structure factor amplitudes were placed on a common scale by internal correlation to yield a data set of 2492 unique reflexions.

Structure Determination

The structure was solved by the heavy-atom method, and was refined by full-matrix least-squares techniques in which the function minimized was $\Sigma w\Delta^2$. A weighting scheme given by $w = (1.00 + 0.101|F_o| + 0.005|F_o|^2)^{-1}$ was used in the latter stages of refinement. Reflexions for which $|F_c| < 0.333|F_o|$ were omitted from the refinement process. Positions for the hydrogen atoms on the pyridine rings were calculated assuming C–H = 1.0 Å. Those on the methylene carbon atoms and water molecules were located from a difference synthesis, the latter positions being optimised at O–H = 0.9 Å. All hydrogen atoms were assigned thermal parameters of $B = 5.0$ Å^2 and were not refined. The refinement process was terminated when the maximum shift in any parameter was less than 0.1σ with 2492 reflexions being included in the final cycle. A final difference map showed no electron density greater than 0.6 eÅ^{-3}. R based on 2492 reflexions was 0.086, and R' $[=(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}]$ was 0.123.

Scattering factors were taken from *International Tables for X-ray Crystallography* [14]. All calculations were carried out on a UNIVAC 1106 computer with programmes written by F.S.S. The refined atomic parameters are given in Tables I–III. A list of final structure factors has been deposited with the Editor.

Discussion

A perspective drawing of the molecule [15], together with the atomic labelling, is given in Fig. 1. Bond lengths and angles are given in Table IV.

Like the several analogous copper(II) chelates previously characterized [8, and references therein] the [Cu(bppn)H_2O] coordination geometry contains the ligand as an approximately planar N_4 tetradentate, with a water molecule occupying the apex of a distorted square-based pyramid. The copper atom is displaced 0.24 Å above the N_4-basal plane (Table V, plane 1) towards the coordinated water molecule, with Cu–O(W1) = 2.268(4) Å. This bond length is shorter than those observed previously in related structures in this series. The Cu–N(*amide*) [average 1.954(5) Å] and Cu–N(*pyridine*) [average 2.065(5) Å] bond lengths are comparable with those of [Cu(bpen)H_2O] [2] but the 5-, 6-, 5-membered chelate ring system generated in the present structure leads to necessary differences in the bond angles at the metal atom [N(*amide*)–Cu–N(*amide*) 93.7(2)°, *cf.* 82.3(3) and 82.8(3)°, and N(*pyridine*)–Cu–N(*pyridine*) 101.1(2)°, *cf.* 112.7(3) and 110.8(3)°].

The two five-membered amide chelate rings (Table V, planes 2 and 3) differ in that one may be considered as planar whereas the second has the Cu atom well out of the plane defined by the other four constituent atoms. The central six-membered chelate ring (Table V, plane 4) adopts a boat conformation, resulting in a closely eclipsed arrangement of the pairs of C(*n*)–C(3) and N(*n*)–Cu bonds. The relevant torsion angles around C(1)–N(1) and C(2)–N(2) are −12.5° and 15.0° respectively.

The relatively small N(*pyridine*)–Cu–N(*pyridine*) bond angle results in a closer contact of the hydrogen atoms in the 6′-positions of the pyridyl rings, with H(15)····H(25) = 1.86 Å. This value is much lower than that observed in the analogous [Cu(bpen)H_2O] 5-,5-,5-membered ring system [2], and a large degree of steric strain in the molecule might be expected as a result. The plane of best fit for pyridyl ring 1 (Table V, plane 5) intersects the N_4 plane (plane 1) at 3.1°. The second pyridyl ring (Table 5, plane 6), however, intersects at 23.4°, indicating a large overall deviation from planarity in the ligand molecule. These two pyridyl planes have a dihedral angle of 26.4°, which signifies rotation in opposite directions relative to the N_4 plane, an arrangement similar to that observed both for the second molecule in the structure of [Cu(bpen)H_2O] [2] and for [Cu(*trans*-bpch)H_2O] H_2O [3]. In fact both picolinamide units in the present structure are closely planar (Table V, planes 9 and 10) and their relative dihedral angle of 26.2° describes the folding between the two basic planes in the molecule. The boat form of the central six-membered chelate ring may be seen as a result of this folding effect.

TABLE IV. Bond Lengths (Å) and Angles (°) with Estimated Standard Deviations in Parentheses.

Cu–O(W1)	2.268(4)		
Cu–N(1)	1.952(4)	Cu–N(2)	1.955(5)
Cu–N(11)	2.074(5)	Cu–N(21)	2.055(4)
C(01)–O(1)	1.268(6)	C(02)–O(2)	1.271(8)
C(01)–C(11)	1.502(7)	C(02)–C(21)	1.487(8)
C(01)–N(1)	1.300(7)	C(02)–N(2)	1.298(7)
C(1)–N(1)	1.472(7)	C(2)–N(2)	1.461(6)
C(1)–C(3)	1.518(8)	C(2)–C(3)	1.499(8)
N(11)–C(11)	1.344(6)	N(21)–C(21)	1.362(8)
C(11)–C(12)	1.374(8)	C(21)–C(22)	1.370(8)
C(12)–C(13)	1.390(9)	C(22)–C(23)	1.395(10)
C(13)–C(14)	1.344(10)	C(23)–C(24)	1.355(11)
C(14)–C(15)	1.380(10)	C(24)–C(25)	1.382(9)
C(15)–N(11)	1.339(7)	C(25)–N(21)	1.346(8)
O(W1)–Cu–N(11)	97.2(2)	O(W1)–Cu–N(21)	91.0(2)
O(W1)–Cu–N(1)	100.1(2)	O(W1)–Cu–N(2)	99.3(2)
N(1)–Cu–N(2)	93.7(2)	N(11)–Cu–N(21)	101.1(2)
N(1)–Cu–N(21)	168.3(2)	N(2)–Cu–N(11)	163.3(2)
N(1)–Cu–N(11)	81.0(2)	N(2)–Cu–N(21)	81.1(2)
Cu–N(11)–C(11)	110.7(4)	Cu–N(21)–C(21)	110.7(3)
Cu–N(11)–C(15)	131.9(4)	Cu–N(21)–C(25)	131.2(4)
Cu–N(1)–C(1)	125.1(4)	Cu–N(2)–C(2)	125.5(4)
Cu–N(1)–C(01)	118.2(4)	Cu–N(2)–C(02)	116.9(4)
C(1)–N(1)–C(01)	116.6(4)	C(2)–N(2)–C(02)	117.6(5)
N(1)–C(01)–O(1)	127.1(6)	N(2)–C(02)–O(2)	126.7(5)
N(1)–C(01)–C(11)	113.4(4)	N(2)–C(02)–C(21)	114.9(5)
C(11)–C(01)–O(1)	119.6(5)	C(21)–C(02)–O(2)	118.4(5)
N(11)–C(11)–C(01)	116.2(5)	N(21)–C(21)–C(02)	114.7(5)
N(11)–C(11)–C(12)	122.2(5)	N(21)–C(21)–C(22)	121.9(5)
C(01)–C(11)–C(12)	121.6(4)	C(02)–C(21)–C(22)	123.2(6)
C(11)–C(12)–C(13)	119.1(5)	C(21)–C(22)–C(23)	118.4(6)
C(12)–C(13)–C(14)	119.2(7)	C(22)–C(23)–C(24)	120.1(5)
C(13)–C(14)–C(15)	118.9(6)	C(23)–C(24)–C(25)	118.9(6)
C(14)–C(15)–N(11)	123.4(5)	C(24)–C(25)–N(21)	122.2(7)
C(15)–N(11)–C(11)	117.2(5)	C(25)–N(21)–C(21)	118.0(5)
N(1)–C(1)–C(3)	110.0(4)	N(2)–C(2)–C(3)	111.4(5)
C(1)–C(3)–C(2)	113.9(4)		

TABLE V. Least-squares Planes Data.

a) Atoms defining and deviations (Å) of relevant atoms from least-squares planes

Plane (1): N(1), N(2), N(11), N(21)
N(1) –0.048, N(2) 0.048, N(11) 0.043, N(21) –0.043, Cu –0.24

Plane (2): N(1), N(11), C(11), C(01)
N(1) –0.022, N(11) 0.022, C(11) –0.038, C(01) 0.038, Cu –0.04

Plane (3): N(2), N(21), C(21), C(02)
N(2) 0.018, N(21) –0.017, C(21) 0.031, C(02) –0.032, Cu 0.27

Plane (4): N(1), N(2), C(1), C(2)
N(1) –0.022, N(2) 0.022, C(1) 0.025, C(2) –0.025, C(3) –0.72, Cu –0.33

(continued on facing page)

TABLE V. *(continued)*

Plane (5): N(11), C(11)–C(15)
N(11), C(13) –0.013, C(11) 0.009, C(12) 0.004, C(14) 0.010, C(15) 0.003, Cu –0.21

Plane (6): N(21), C(21)–C(25)
N(21) 0.043, C(21) –0.021, C(22) –0.015, C(23) 0.030, C(24) –0.009, C(25) –0.029, Cu 0.32

Plane (7): C(11), N(1), O(1), C(01)
C(11), N(1), O(1) <0.001, C(01) –0.002

Plane (8): C(21), N(2), O(2), C(02)
C(21), N(2), O(2) –0.001, C(02) 0.003

Plane (9): N(11), C(11)–C(15), C(01), O(1), N(1)
N(11) 0.027, C(11) –0.022, C(12) –0.071, C(13) –0.059, C(14) 0.034, C(15), 0.068, C(01) 0.003, O(1) 0.128, N(1) –0.106, Cu –0.12

Plane (10): N(21), C(21)–C(25), C(02), O(2), N(2)
N(21) 0.054, C(21) 0.073, C(22) 0.085, C(23) 0.048, C(24) –0.074, C(25) –0.096, C(02) –0.007, O(2) –0.139, N(2) 0.056, Cu 0.35

Plane (11): N(11), C(11), C(12), C(13)
N(11) –0.001, C(11) 0.002, C(12) –0.002, C(13) 0.001, C(14) 0.04, C(15) 0.03

Plane (12): N(11), C(13), C(14), C(15)
N(11) –0.002, C(13) –0.001, C(14) 0.003, C(15) –0.003, C(11), C(12) 0.04

Plane (13): N(21), C(21), C(22), C(23)
N(21) 0.003, C(21) –0.006, C(22) 0.005, C(23) –0.003, C(24) –0.10, C(25) –0.12

Plane (14): N(21), C(23), C(24), C(25)
N(21) 0.006, C(23) –0.005, C(24) 0.011, C(25) –0.011, C(21), C(22) –0.11

Plane (15): N(11), C(11), C(15)
Cu 0.14

Plane (16): C(12), C(13), C(14)

Plane (17): N(21), C(21), C(25)
Cu 0.08

Plane (18): C(22), C(23), C(24)

b) Dihedral angles (°) between relevant planes

1–2	6.1	5–6	26.4
1–3	21.4	5–7	8.9
1–4	5.2	6–8	9.6
1–5	3.1	9–10	26.2
1–6	23.4	11–12	1.9
1–9	5.9	13–14	5.3
1–10	20.6	15–16	3.2
		17–18	9.1

c) Equations of the planes in the form $lX' + mY' + nZ' - p = 0$ where X', Y' and Z' are orthogonal coordinates related to the coordinates X, Y and Z by $X' = X \sin\beta$, $Y' = Y$ and $Z' = Z + X \cos\beta$.

	l	*m*	*n*	*p*
Plane (1):	–0.4507	0.7102	0.5408	1.3326
Plane (2):	–0.5402	0.7135	0.4462	0.7024

(continued overleaf)

TABLE V. *(continued)*

Plane (3):	–0.1751	0.6567	0.7336	1.8452
Plane (4):	–0.4768	0.6590	0.5817	1.4348
Plane (5):	–0.4862	0.7162	0.5007	1.1286
Plane (6):	–0.0897	0.6831	0.7248	1.9677
Plane (7):	–0.5484	0.7527	0.3643	0.3013
Plane (8):	–0.2529	0.6441	0.7219	1.8200
Plane (9):	–0.5035	0.7345	0.4550	0.9011
Plane (10):	–0.1543	0.6598	0.7354	1.8164
Plane (11):	–0.4819	0.7271	0.4890	1.1121
Plane (12):	–0.4900	0.7049	0.5128	1.1222
Plane (13):	–0.1326	0.6687	0.7316	1.9163
Plane (14):	–0.0464	0.6986	0.7140	2.0952
Plane (15):	–0.5081	0.7110	0.4861	0.9757
Plane (16):	–0.4615	0.7215	0.5161	1.3507
Plane (17):	–0.1236	0.7437	0.6570	2.0084
Plane (18):	–0.0681	0.6412	0.7644	1.8195

TABLE VI. Contact Distances (Å) with Estimated Deviations in Parentheses.

a) proposed Hydrogen Bonds		
	Acceptor at	
O(W1)–H(W11)···O(2)	$1 + x, y, z$	2.754(7)
O(W1)–H(W12)···O(2)	$\bar{x}, \bar{y}, \bar{z}$	2.806(7)
O(W2)–H(W21)···O(1)	x, y, z	2.886(7)
O(W2)–H(W22)···O(W3)	$x - 1, y, z$	2.883(8)
O(W3)–H(W31)···O(1)	x, y, z	2.807(6)
O(W3)–H(W32)···O(W2)	$1 - x, \bar{y}, 1 - z$	2.832(8)
b) Intermolecular Distances <3.5 Å		
O(W1)··········C(2)	at $1 + x, y, z$	3.411(8)
O(W3)··········C(22)	at $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$	3.449(7)
O(W3)··········C(24)	at $1\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$	3.460(8)
O(W3)··········C(25)	at $1\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$	3.393(7)
O(W3)··········C(15)	at $1\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$	3.436(7)
O(2)··········C(15)	at $x - 1, y, z$	3.221(8)
O(2)··········C(25)	at $x - 1, y, z$	3.395(8)

Severe steric strain enforced in the structure of [Cu(6-mebpb)] was observed to result in a boat form of distortion in the constituent pyridyl rings [6]. A close inspection of atomic deviations from the mean planes of those rings in the present structure (Table V, planes 5 and 6) demonstrates the presence of a similar effect. The corresponding folding angles, γ and δ [6], are 3.2° and 1.9° for ring 1, and for ring 2 9.1° and 5.3° (Table V, planes 11–18). Thus the distortion observed in the latter pyridyl ring is greater than that enforced by steric hindrance in [Cu(6-mebpb)] [6]. This fact once again demonstrates the severe 'B-strain' effect resulting from planar coordination of a tetradentate ligand of this geometry [10]. In contrast, the amide nitrogen atoms show only minor distortions from planarity (2.8 and 1.0% respectively).

In each of the Cu(bis-*amide*)H_2O structures reported previously in this series a pronounced tendency for planar crystal packing was observed. Such a layered arrangement is not present in this structure, as is demonstrated in Fig. 2, although this may prove to be a feature of the structure of the α-form not yet investigated. The lattice and coordinated water molecules are involved in a hydrogen bonding network which includes the amide oxygen atoms and gives rise to sheets perpendicular to b (Fig. 2). Details are given in Table VI. There is no close contact to the metal atom in what would constitute six-coordination. Intermolecular distances less than 3.5 Å

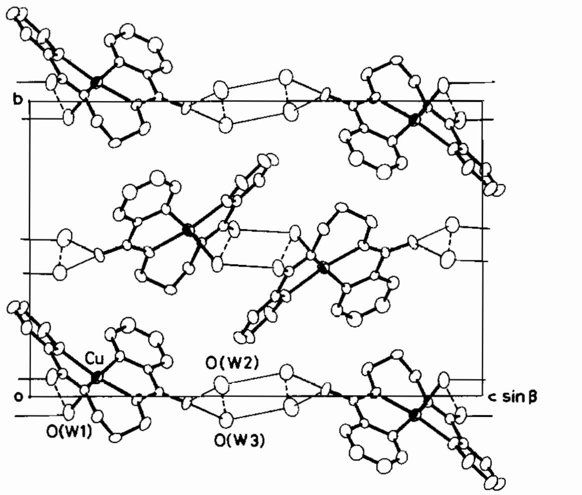

Fig. 2. The packing of the molecules in the crystal showing the hydrogen bonding network. Broken lines indicate that one of the atoms involved in the bond is a lattice translation away in *a*. The labelling of the water molecules also is shown.

also are shown in Table VI, where it may be seen that the α-pyridyl carbon atoms C(15) and C(25) have several close contacts to oxygen atoms.

References

1 R. L. Chapman, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 43,* 29 (1980).
2 R. L. Chapman, F. S. Stephens and R. S. Vagg, *Acta Cryst., B37,* 75 (1981).
3 M. Mulqi, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 51,* 9 (1981).
4 F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 51,* 149 (1981).
5 M. Mulqi, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 52,* 73 (1981).
6 R. L. Chapman, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 52,* 169 (1981).
7 M. Mulqi, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 52,* 177 (1981).
8 F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 57,* 9(1982).
9 D. J. Barnes, R. L. Chapman, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 51,* 155 (1981).
10 J. G. Gibson and E. D. McKenzie, *J. Chem. Soc. (A),* 1666 (1971).
11 D. J. Barnes, R. L. Chapman, R. S. Vagg and E. C. Watton, *J. Chem. Eng. Data, 23,* 349 (1978).
12 H. Ojima, *Nippon Kagaku Zasshi, 88,* 333 (1967).
13 W. H. Saxby, F. S. Stephens and R. S. Vagg, in preparation.
14 'International Tables for X-ray Crystallography', Vol. IV, pp. 72–79, Kynoch Press, Birmingham (1974).
15 C. K. Johnson, ORTEP, (1965). Report ORNL-3794, revised 1971. Oak Ridge National Laboratory, Tennessee.