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

FREDERICK S. STEPHENS and ROBERT S. VAGG

School of Chemistry, Macquarie University, North Ryde, N.S.W. 2113, Australia

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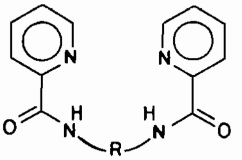
α-Aqua[N,N′-bis(2′-pyridinecarboxamido)-1,3-propane]copper(II) dihydrate, $C_{15}H_{20}N_4O_5Cu$*, is monoclinic, space group* $P2_1/c$*, with* $a = 11.719(2)$*,* $b = 13.092(2)$*,* $c = 12.663(2)$ *Å,* $\beta = 119.56(1)°$*,* $Z = 4$*. The structure was refined to* $R = 0.026$ *for 2398 diffractometer data using full-matrix least-squares methods. The copper atom is five-coordinate with the* N_4*-tetradentate ligand encompassing the base of a distorted square-based pyramid which is appreciably distorted towards a trigonal bipyramid [average Cu–N(amide) 1.950(2), Cu–N(pyridine) 2.043(2) Å, N(amide)–Cu–N(amide) 94.5(1), N(pyridine)–Cu–N(pyridine) 100.2(1)°] and with the copper atom lying 0.27 Å above the* N_4 *plane towards the apical water molecule [Cu–O 2.236(2) Å]. The central six-membered chelate ring adopts a skewed boat conformation and the enforced strain in the molecule results in non-planar distortions in the pyridine rings with only small distortions in the amide groups. The molecules pack in sheets parallel to* $(10\bar{1})$ *and the hydrogen-bonding network involves the water molecules and the amide oxygen atoms of the ligand.*

Introduction

The bivalent copper complexes of the deprotonated bis-picolinamide ligands investigated thus far have shown that in the solid state two molecular complexes co-crystallise for $bpenH_2$, **I** [1], and for *trans*-$bpchH_2$, **II**, two different hydrate forms crystallise [2, 3]. The metal environments in these structures are essentially similar, being square-based pyramidal with the tetradentate ligand encompassing the base and a water molecule occupying the apex, and differences between like complexes being in the ligand conformations. In particular, one form shows amide N atoms with significantly larger pyramidal distortion.

For the related ligand N,N′-bis(2′-pyridinecarboxamide)-1,3-propane ($bppnH_2$), **III**, two crystalline forms of the compound $Cu(bppn)\cdot 3H_2O$ separate from aqueous solution [4].



(I) $R = -CH_2CH_2-$

(II) $R = -\{CH(CH_2)_4CH\}-$

(III) $R = -CH_2CH_2CH_2-$

Initially deep-blue rhomboids crystallise, designated the α-form, and then on prolonged standing long blue needles, the β-form, separate and redissolution of either form yields solutions of identical physical properties [5]. The crystal structure of the β-form has been recently reported [4] in which the crystal packing is significantly at variance with that reported for other $[Cu(bis\text{-}amide)H_2O]$ structures in this series. We now report the structure analysis of the α-form.

Experimental

Crystal Data

$C_{15}H_{20}N_4O_5Cu$, $Mr = 400.1$, Monoclinic, $a = 11.719(2)$, $b = 13.092(2)$, $c = 12.663(2)$ Å, $\beta = 119.56(1)°$, $U = 1689.9$ Å^3, $Z = 4$, $D_c = 1.572$ Mg m^{-3}, $F(000) = 828$, $\mu(\text{Mo-}K_\alpha) = 1.33$ mm^{-1}. Systematic absences: $0k0$ if $k \neq 2n$ and $h0l$ if $l \neq 2n$. Space group $P2_1/c$ (No. 14).

Initially unit cell parameters were determined from single crystal oscillation and Weissenberg photographs using Cu-K_α radiation. Accurate cell parameters were obtained from a least-squares fit to diffractometer data. Intensities were collected on an Enraf-Nonius CAD4 diffractometer using graphite monochromatised Mo-K_α radiation. Of the 2965 reflexions recorded 2398 gave counts for which $I > 3\sigma(I)$ and these were used for the structure determination. The intensities were corrected for Lorentz, polarisation and absorption effects.

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*Part XVI, M. Mulqi, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 63,* 197 (1982).

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TABLE I. Final Atomic Coordinates (fractional $\times 10^4$) for the Non-hydrogen Atoms with Estimated Standard Deviations in Parentheses.

	x	y	z
Cu	1832.0(2)	4307.2(2)	4284.9(2)
O(W1)	2667(2)	3080(2)	3477(2)
O(W2)	5583(2)	3376(2)	901(2)
O(W3)	2961(2)	1218(2)	4575(3)
O(1)	–2037(2)	4427(2)	1856(2)
O(2)	4511(2)	6559(1)	5298(2)
N(1)	197(2)	4620(2)	2811(2)
N(2)	2766(2)	5492(1)	4153(2)
N(11)	554(2)	3552(2)	4691(2)
N(21)	3519(2)	4168(1)	5888(2)
C(1)	87(3)	5255(2)	1808(2)
C(2)	2311(3)	6103(2)	3047(2)
C(3)	1419(3)	5471(2)	1930(2)
C(O1)	–890(2)	4280(2)	2723(2)
C(O2)	3814(2)	5778(2)	5141(2)
C(11)	–701(2)	3660(2)	3799(2)
C(12)	–1727(3)	3244(2)	3883(2)
C(13)	–1488(3)	2687(2)	4897(2)
C(14)	–222(3)	2579(2)	5809(3)
C(15)	771(3)	3035(2)	5683(3)
C(21)	4221(2)	5038(2)	6181(2)
C(22)	5260(2)	5210(2)	7324(2)
C(23)	5628(3)	4444(2)	8192(2)
C(24)	4976(2)	3523(2)	7859(2)
C(25)	3940(2)	3409(2)	6708(2)

Neutral-atom scattering factors were taken from International Tables for X-ray Crystallography [6]. All calculations were carried out on a UNIVAC 1106 computer with programmes written by F.S.S.

The structure was solved by the heavy-atom method and refined by a full-matrix least-squares procedure in which the function minimised was $w\Delta^2$. The weight, w, for each reflexion was initially given by $w = 1/|F_o|$ and in the final stages was that obtained from counting statistics. The refinement included the atomic parameters for all atoms with anisotropic thermal parameters for the non-hydrogen atoms. Refinement was terminated when the maximum shift in any parameter was $<0.2\sigma$. The final value for R was 0.026 and R' [= $\{\Sigma w\Delta^2/\Sigma w|F_o|^2\}^{1/2}$] was 0.035. A final difference map showed densities of –0.45 to 0.25 eÅ^{-3} the larger negative values being associated with the copper atom. The final atomic parameters are given in Tables I–III. A list of structure factors has been deposited with the Editor.

Discussion

The bond lengths and angles are given in Table IV. Figure 1 shows a perspective drawing [7] of the chelate molecule together with the atom labelling. The molecular packing and the hydrogen-bonding in

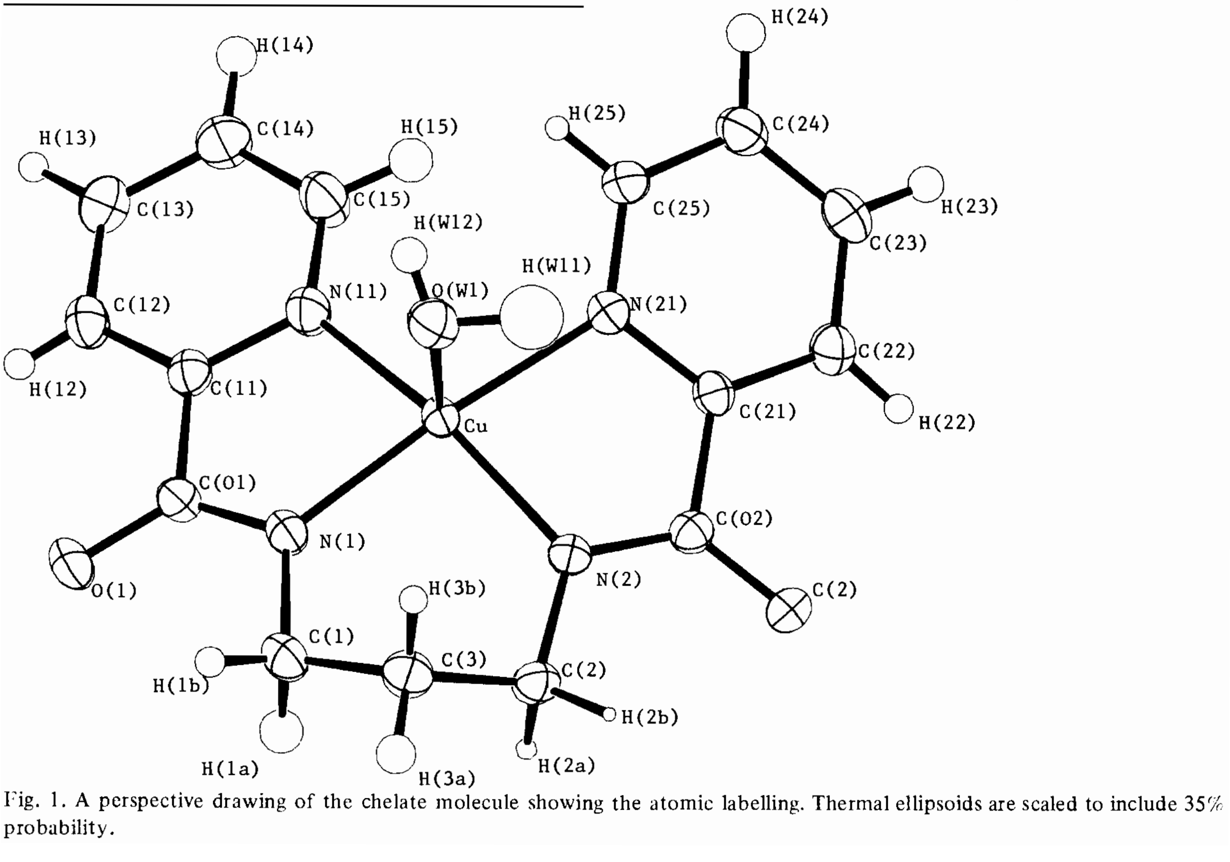

Fig. 1. A perspective drawing of the chelate molecule showing the atomic labelling. Thermal ellipsoids are scaled to include 35% probability.

TABLE II. 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	45.6(3)	39.0(2)	43.8(3)	−5.3(2)	11.6(2)	8.0(2)
O(W1)	77(2)	45(1)	76(2)	4(1)	23(2)	0(1)
O(W2)	64(2)	54(2)	97(2)	1(1)	21(2)	−17(1)
O(W3)	75(2)	49(1)	137(3)	−6(2)	20(2)	−1(2)
O(1)	51(2)	73(2)	87(2)	−2(1)	7(2)	28(1)
O(2)	72(2)	35(1)	67(2)	−9(1)	24(1)	4(1)
N(1)	51(2)	47(1)	50(2)	−2(1)	15(2)	10(1)
N(2)	59(2)	36(1)	45(2)	−3(1)	22(2)	5(1)
N(11)	58(2)	54(1)	60(2)	−6(1)	23(2)	11(1)
N(21)	54(2)	37(1)	53(2)	0(1)	22(1)	5(1)
C(1)	69(3)	60(2)	53(2)	−5(2)	12(2)	16(2)
C(2)	74(3)	38(2)	53(2)	−3(2)	33(2)	6(1)
C(3)	86(3)	52(2)	50(2)	−6(2)	30(2)	8(2)
C(O1)	61(2)	39(1)	53(2)	3(2)	16(2)	3(1)
C(O2)	58(2)	32(1)	53(2)	1(1)	30(2)	−1(1)
C(11)	59(2)	34(1)	58(2)	0(1)	27(2)	−6(1)
C(12)	53(3)	47(2)	66(2)	0(2)	27(2)	−5(2)
C(13)	76(3)	54(2)	75(2)	−7(2)	50(2)	−8(2)
C(14)	89(3)	64(2)	73(3)	−5(2)	45(2)	13(2)
C(15)	65(3)	85(2)	66(2)	−5(2)	24(2)	25(2)
C(21)	48(2)	37(1)	50(2)	2(1)	25(2)	−1(1)
C(22)	69(3)	45(2)	57(2)	−5(2)	23(2)	−6(2)
C(23)	73(3)	64(2)	46(2)	5(2)	16(2)	2(2)
C(24)	70(3)	55(2)	61(2)	7(2)	29(2)	15(2)
C(25)	65(3)	42(2)	68(2)	−1(2)	30(2)	13(2)

TABLE III. Atomic Parameters for the Hydrogen Atoms (coordinates $\times 10^3$) with Estimated Standard Deviations in Parentheses.

	x	y	z	B (Å^2)
H(1a)	−33(3)	591(3)	180(3)	2.3(7)
H(1b)	−43(3)	493(2)	108(3)	1.2(5)
H(2a)	184(2)	671(2)	308(2)	0.5(5)
H(2b)	306(2)	637(2)	301(2)	0.2(4)
H(3a)	128(3)	583(2)	119(3)	1.9(6)
H(3b)	185(2)	482(2)	196(2)	1.0(5)
H(12)	−246(3)	335(2)	334(3)	1.2(6)
H(13)	−221(2)	240(2)	501(2)	1.1(5)
H(14)	−4(3)	217(2)	655(3)	2.0(6)
H(15)	166(3)	300(2)	632(3)	2.4(6)
H(22)	568(3)	581(2)	746(2)	1.1(6)
H(23)	633(3)	454(2)	896(3)	1.6(6)
H(24)	523(3)	291(2)	841(3)	1.9(6)
H(25)	351(2)	280(2)	648(2)	0.7(5)
H(W11)	366(4)	323(3)	390(4)	5.0(9)
H(W12)	262(3)	256(3)	367(3)	1.6(8)
H(W21)	622(3)	367(2)	144(3)	1.7(5)
H(W22)	565(3)	280(3)	63(3)	3.1(8)
H(W31)	279(4)	71(3)	408(3)	3.4(9)
H(W32)	376(4)	120(3)	494(3)	3.3(8)

the cell are shown in Fig. 2. Table V lists the proposed hydrogen bond distances and other intermolecular contacts <3.5 Å. The hydrogen-bond network involves both the coordinated and lattice water molecules together with the oxygen atoms of the amide groups of the ligand. The coordinated water molecule hydrogen-bonds an amide oxygen atom of a neighbouring molecule and a lattice water molecule. The overall donor-acceptor arrangement is similar to that found in [Cu(*trans*-bpch)H_2O]·$2H_2O$ [3] but with the chelate molecules forming layers parallel to ($10\bar{1}$). This contrasts with the network found in the analogous β-form [4] in which the coordinated water molecule hydrogen-bonds identical amide oxygen atoms of two neighbouring chelate molecules whereas the lattice water molecules hydrogen-bond both to each other and to the same amide oxygen atom of an adjacent chelate molecule.

The bonding parameters in the present structure closely parallel those in the β-form [4]: a comparison of relevant parameters is given in Table VI. The copper atom has a distorted square-based pyramidal environment with a water molecule occupying the apex and with the copper atom displaced 0.27 Å from the N_4-basal plane (Table VII, plane 1) towards the apex. However in the present structure there is a marked shift towards trigonal bipyramidal stereochemistry (*ca.* 30% compared with 10% for the β-form) as defined by the dihedral angles between the N_3-planes (Table

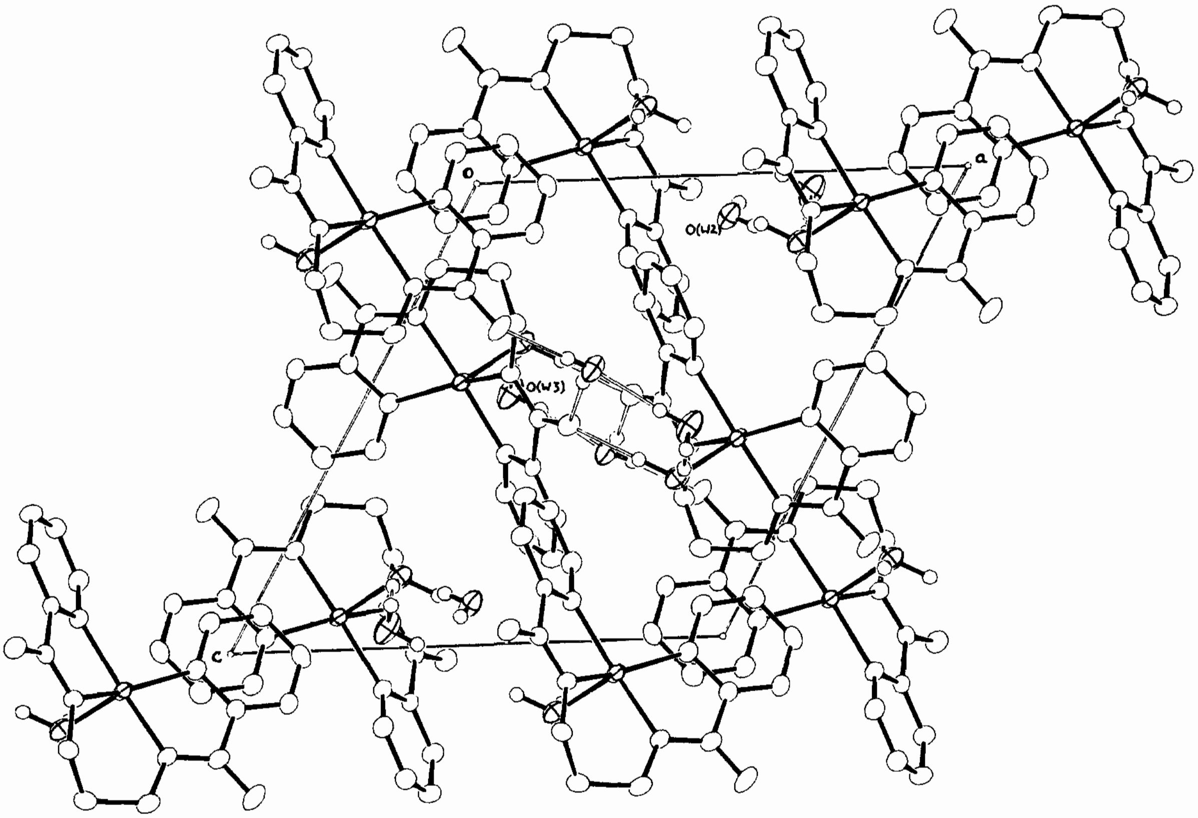

Fig. 2. The packing of the molecules in the crystal showing the hydrogen-bonding network. The labelling of the water molecules also is shown.

TABLE IV. Bond Lengths and Angles with Estimated Standard Deviations in Parentheses.

a) Distances (Å)

	Cu–O(W1)	2.361(2)	
Cu–N(1)	1.948(2)	Cu–N(2)	1.952(2)
Cu–N(11)	2.060(2)	Cu–N(21)	2.026(2)
C(O1)–O(1)	1.262(3)	C(O2)–O(2)	1.262(3)
C(O1)–C(11)	1.506(3)	C(O2)–C(21)	1.509(3)
C(O1)–N(1)	1.301(3)	C(O2)–N(2)	1.304(3)
C(1)–N(1)	1.470(3)	C(2)–N(2)	1.466(3)
C(1)–C(3)	1.517(4)	C(2)–C(3)	1.522(3)
N(11)–C(11)	1.349(3)	N(21)–C(21)	1.345(3)
C(11)–C(12)	1.370(3)	C(21)–C(22)	1.374(3)
C(12)–C(13)	1.380(4)	C(22)–C(23)	1.390(4)
C(13)–C(14)	1.366(4)	C(23)–C(24)	1.377(4)
C(14)–C(15)	1.386(4)	C(24)–C(25)	1.369(4)
C(15)–N(11)	1.336(3)	C(25)–N(21)	1.344(3)
C(1)–H(1a)	0.99(3)	C(12)–H(12)	0.81(3)
C(1)–H(1b)	0.92(3)	C(13)–H(13)	1.00(3)
C(2)–H(2a)	0.98(3)	C(14)–H(14)	1.01(3)
C(2)–H(2b)	0.96(2)	C(15)–H(15)	0.95(3)
C(3)–H(3a)	0.98(3)	C(22)–H(22)	0.89(3)
C(3)–H(3b)	0.98(3)	C(23)–H(23)	0.92(3)
O(W1)–H(W11)	1.03(4)	C(24)–H(24)	1.00(3)
O(W1)–H(W12)	0.73(3)	C(25)–H(25)	0.90(3)
O(W2)–H(W21)	0.76(3)	O(W3)–H(W31)	0.87(4)
O(W2)–H(W22)	0.85(4)	O(W3)–H(W32)	0.81(3)

(continued on facing page)

TABLE IV. *(continued)*

b) Angles (°)

O(W1)–Cu–N(1)	98.6(1)	O(W1)–Cu–N(2)	97.7(1)
O(W1)–Cu–N(11)	106.8(1)	O(W1)–Cu–N(21)	88.0(1)
N(1)–Cu–N(2)	94.5(1)	N(11)–Cu–N(21)	100.2(1)
N(1)–Cu–N(21)	172.6(1)	N(2)–Cu–N(11)	155.5(1)
N(1)–Cu–N(11)	81.2(1)	N(2)–Cu–N(21)	81.1(1)
Cu–N(11)–C(11)	111.6(2)	Cu–N(21)–C(21)	111.2(1)
Cu–N(11)–C(15)	130.7(2)	Cu–N(21)–C(25)	130.2(2)
Cu–N(1)–C(1)	124.9(2)	Cu–N(2)–C(2)	124.1(2)
Cu–N(1)–C(O1)	118.0(2)	Cu–N(2)–C(O2)	116.7(2)
C(1)–N(1)–C(O1)	117.1(2)	C(2)–N(2)–C(O2)	119.1(2)
N(1)–C(O1)–O(1)	126.9(2)	N(2)–C(O2)–O(2)	127.9(2)
N(1)–C(O1)–C(11)	114.0(2)	N(2)–C(O2)–C(21)	113.3(2)
C(11)–C(O1)–O(1)	119.2(2)	C(21)–C(O2)–O(2)	118.7(2)
N(11)–C(11)–C(O1)	115.2(2)	N(21)–C(21)–C(O2)	114.6(2)
N(11)–C(11)–C(12)	122.0(2)	N(21)–C(21)–C(22)	122.1(2)
C(O1)–C(11)–C(12)	122.8(2)	C(O2)–C(21)–C(22)	123.3(2)
C(11)–C(12)–C(13)	119.9(2)	C(21)–C(22)–C(23)	118.9(2)
C(12)–C(13)–C(14)	118.7(2)	C(22)–C(23)–C(24)	118.7(2)
C(13)–C(14)–C(15)	118.8(3)	C(23)–C(24)–C(25)	119.2(2)
C(14)–C(15)–N(11)	123.0(3)	C(24)–C(25)–N(21)	122.4(2)
C(15)–N(11)–C(11)	117.6(2)	C(25)–N(21)–C(21)	118.2(2)
N(1)–C(1)–C(3)	111.8(2)	N(2)–C(2)–C(3)	110.5(2)
C(1)–C(3)–C(2)	113.4(2)		
Cu–O(W1)–H(W11)	104(2)	C(1)–C(3)–H(3a)	108(2)
Cu–O(W1)–H(W12)	112(2)	C(1)–C(3)–H(3b)	109(1)
H(W11)–O(W1)–H(W12)	105(3)	C(2)–C(3)–H(3a)	110(2)
H(W21)–O(W2)–H(W22)	110(3)	C(2)–C(3)–H(3b)	109(1)
H(W31)–O(W3)–H(W32)	110(3)	H(3a)–C(3)–H(3b)	107(2)
N(1)–C(1)–H(1a)	109(2)	N(2)–C(2)–H(2a)	110(1)
N(1)–C(1)–H(1b)	110(2)	N(2)–C(2)–H(2b)	109(1)
C(3)–C(1)–H(1a)	108(2)	C(3)–C(2)–H(2a)	110(1)
C(3)–C(1)–H(1b)	109(2)	C(3)–C(2)–H(2b)	112(1)
H(1a)–C(1)–H(1b)	108(2)	H(2a)–C(2)–H(2b)	105(2)
C(11)–C(12)–H(12)	119(2)	C(21)–C(22)–H(22)	118(2)
C(13)–C(12)–H(12)	122(2)	C(23)–C(22)–H(22)	123(2)
C(12)–C(13)–H(13)	122(1)	C(22)–C(23)–H(23)	120(2)
C(14)–C(13)–H(13)	119(1)	C(24)–C(23)–H(23)	121(2)
C(13)–C(14)–H(14)	119(2)	C(23)–C(24)–H(24)	124(2)
C(15)–C(14)–H(14)	122(2)	C(25)–C(24)–H(24)	117(2)
C(14)–C(15)–H(15)	121(2)	C(24)–C(25)–H(25)	118(2)
N(11)–C(15)–H(15)	116(2)	N(21)–C(25)–H(25)	120(2)

VII, planes 19–22). The Cu–OH_2 distance of 2.236(2) Å is the shortest yet observed in related structures for this series and it might be viewed as a result of the pronounced distortion towards trigonal bipyramidal stereochemistry. This distortion results from a larger tetrahedral-type twist of 11° (3° for the β-form) for the picolinamide groups relative to one another. This twisting has two further consequences: firstly, it alleviates the steric effects of the 6–6′ protons present in the β-form whilst still maintaining the relatively small $N_{pyridine}$–Cu–$N_{pyridine}$ angle (Table VI); and secondly, it gives rise to larger N_4/pyridine and pyridine/pyridine dihedral angles.

The boat conformation of the central chelate ring (Table VII, plane 4) again results from the folding of the two closely planar picolinamide units (Table VII, planes 9 and 10). However, the dihedral angle of 40.0° between the planes of these units is considerably larger than that of 26.2° in the β-form [4] and further this together with the increased twist causes a skewing in the conformation as shown by the increased torsion angle around C(2)–N(2) (Table VI).

Once again there is evidence in the present structure of a boat form of distortion in the pyridyl rings as was observed in the highly strained structure of Cu(6-mebpb) [8]. The values of the folding

TABLE V.* Contact Distances (Å) with Estimated Standard Deviations in Parentheses.

a) Proposed hydrogen bonds (angles in °)

	O···O	H···O	∠O–H···O
O(W1)–H(W11)····O(2^{III})	2.917(3)	1.89(4)	177(2)
O(W1)–H(W12)····O(W3)	2.742(3)	2.02(3)	165(3)
O(W2)–H(W21)····O(1^{I})	2.794(3)	2.03(3)	177(2)
O(W2)–H(W22)····O(2^{VII})	2.795(3)	1.96(4)	168(2)
O(W3)–H(W31)····O(1^{VI})	2.831(3)	1.99(4)	162(2)
O(W3)–H(W32)····O(W2^{IV})	2.731(4)	1.95(4)	161(3)

b) Intermolecular Distances <3.5 Å

O(W3)····C(1^{VI})	3.353(4)	O(2)····C(24^{VIII})	3.321(3)
O(W3)····C(23^{IX})	3.394(4)	N(2)····C(13^{II})	3.340(3)
O(W2)····C(22^{III})	3.413(3)	C(O2)··C(13^{II})	3.367(3)
O(W1)····C(15^{V})	3.439(3)	O(2)····N(21^{III})	3.452(2)
O(W2)····C(25^{V})	3.487(3)	C(O2)··C(12^{II})	3.483(3)

*Roman numeral superscripts refer to the following equivalent positions relative to x, y, z:

I	$1+x, y, z$	IV	$x, \frac{1}{2}-y, \frac{1}{2}+z$	VII	$1-x, y-\frac{1}{2}, \frac{1}{2}-z$
II	$-x, 1-y, 1-z$	V	$x, \frac{1}{2}-y, z-\frac{1}{2}$	VIII	$1-x, \frac{1}{2}+y, 3/2-z$
III	$1-x, 1-y, 1-z$	VI	$-x, y-\frac{1}{2}, \frac{1}{2}-z$	IX	$1-x, y-\frac{1}{2}, 3/2-z$

TABLE VI. Comparison of the Structures of the α- and β-forms of [Cu(bppn)H_2O]·$2H_2O$ (distances in Å and angles in °).

	α-form	β-form
Cu–OH_2	2.236(2)	2.268(4)
Cu–N_{amide}	1.950(2)	1.954(5)
Cu–$N_{pyridine}$	2.043(2)	2.065(5)
N_{amide}–Cu–N_{amide}	94.5(1)	93.7(2)
$N_{pyridine}$–Cu–$N_{pyridine}$	100.2(1)	101.1(2)
H(15)····H(25)	2.10(4)	1.84
N_{amide}Distortion (%)	4.8, 7.0	2.8, 1.0
Dihedral Angles (°)		
N_4/pyridine(1)	12.9	3.1
N_4/pyridine(2)	30.6	23.4
pyridine(1)/pyridine(2)	43.4	26.4
pyridine(1) γ, δ*	2.0, 1.2	3.2, 1.9
pyridine(2) γ, δ	8.4, 5.0	9.1, 1.0
Torsion Angles (°)		
C(3)–C(1)/C(1)–N(1)	–12.5	–11.3
C(3)–C(2)/C(2)–N(2)	15.0	24.5
Reference	this work	[4]

*Folding angles for a pyridine ring as defined in ref. [8].

angles (Table VI) observed in the α- and β-forms are closely comparable and again demonstrate the severe 'B-strain' effect resulting from the planar coordination of such a tetradentate ligand [9]. However, in the present structure there is a significant, but small, distortion from planarity of the amide nitrogen atoms.

The β-form is clearly more thermodynamically stable since recrystallisation of the rhomboids results in this form [5]. The less thermodynamically stable

TABLE VII. Least-squares Planes and Their Equations given by $lX' + mY' + nZ' - p = 0$ where X', Y', and Z' are Orthogonal Coordinates (A) derived with *respect* to the Orthogonal Axes a', b, c. Deviations (A) of relevant atoms from the planes are given in square brackets.

	l	*m*	*n*	*p*
Plane (1): N(1), N(2), N(11), N(21)	−0.2465	0.7231	0.6453	6.7058
[N(1) −0.16; N(2) 0.16; N(11) 0.14; N(21) −0.15; Cu −0.27; O(W1) −2.61]				
Plane (2): N(1), N(11), C(11), C(O1)	−0.0801	0.8319	0.5492	6.9087
[N(1), C(11) −0.001; N(11), C(O1) 0.001; Cu 0.03]				
Plane (3): N(2), N(21), C(21), C(O2)	−0.5997	0.4354	0.6715	3.8809
[N(2) 0.016; N(21) −0.016; C(21) 0.027; C(O2) −0.028; Cu 0.39]				
Plane (4): N(1), N(2), C(1), C(2)	−0.3855	0.7108	0.5883	6.2134
[N(1) 0.036; N(2) −0.036; C(1) −0.041; C(2) 0.041; C(3) −0.72; Cu −0.36]				
Plane (5): N(11), C(11)–C(15)	−0.0849	0.8379	0.5391	6.8886
[N(11) −0.010; C(11) −0.001; C(12) 0.008; C(13) −0.005; C(14) −0.006; C(15) 0.014; Cu 0.03; C(O1) 0.02]				
Plane (6): N(21), C(21)–C(25)	−0.6186	0.3526	0.7021	3.4722
[N(21) 0.040; C(21) −0.027; C(22) −0.008; C(23) 0.028; C(24) −0.016; C(25) −0.018; Cu 0.43; C(O2) −0.19]				
Plane (7): C(11), N(1), O(1), C(O1)	−0.0723	0.8305	0.5524	6.9110
[C(11), N(1), O(1) 0.001; C(O1) −0.003]				
Plane (8): C(21), N(2), O(2), C(O2)	−0.5603	0.5058	0.6560	4.4614
[C(21) −0.003; N(2), O(2) −0.004; C(O2) 0.011]				
Plane (9): N(11), C(11)–C(15), C(O1), O(1), N(1)	−0.0804	0.8346	0.5450	6.9116
[N(11), C(11) −0.013; C(12) −0.002; C(13) −0.006; C(14) 0.003; C(15) 0.020; C(O1) −0.003; O(1) 0.015; N(1) −0.002; Cu 0.02; C(1) 0.04; N(2) 0.86]				
Plane (10): N(21), C(21)–C(25), C(O2), O(2), N(2)	−0.6071	0.4184	0.6756	3.7158
[N(21) 0.053; C(21) 0.071; C(22) 0.094; C(23) 0.045; C(24) −0.085; C(25) −0.087; C(O2) −0.002; O(2) −0.143; N(2) 0.054; Cu 0.46; C(2) −0.10; N(1) 1.02]				
Plane (11): N(11), C(11), C(12), C(13)	−0.0764	0.8355	0.5442	6.8990
[N(11) 0.001; C(11) −0.003; C(12) 0.003; C(13) −0.001; C(14) 0.012; C(15) 0.034]				
Plane (12): N(11), C(13), C(14), C(15)	−0.0924	0.8409	0.5333	6.8597
[N(11) −0.005; C(13) 0.004; C(14) −0.009; C(15) 0.009; C(11) 0.017; C(12) 0.029]				
Plane (13): N(21), C(21), C(22), C(23)	−0.6126	0.3922	0.6862	3.6582
[N(21) 0.005; C(21) −0.011; C(22) −0.005; C(23) 0.010; C(24) −0.101; C(25) −0.102]				
Plane (14): N(21), C(23), C(24), C(25)	−0.6215	0.3121	0.7186	3.3680
[N(21) 0.002; C(23) −0.002; C(24) 0.004; C(25) −0.004; C(21) −0.113; C(22) −0.092]				
Plane (15): N(11), C(11), C(15)	−0.0712	0.8497	0.5225	6.8473
[Cu 0.09]				
Plane (16): C(12), C(13), C(14)	−0.0881	0.8319	0.5479	6.9289
Plane (17): N(21), C(21), C(25)	−0.5463	0.3667	0.7530	4.1239
[Cu 0.21]				
Plane (18): C(22), C(23), C(24)	−0.6627	0.3410	0.6668	2.9289
Plane (19): N(11), N(2), N(1)	−0.3718	0.7511	0.5455	6.3484
[Cu 0.43]				
Plane (20): N(11), N(2), N(21)	−0.1333	0.6770	0.7238	7.1406
[Cu 0.41]				
Plane (21): N(21), N(1), N(2)	−0.3217	0.6012	0.7315	6.0927
[Cu 0.11]				
Plane (22): N(21), N(1), N(11)	−0.1808	0.8131	0.5533	6.7887
[Cu 0.13]				

Dihedral Angles (°)

1–2	12.7	5–6	43.4	11–12	1.2	19–20	17.7
1–3	26.4	5–7	1.1	13–14	5.0	21–22	17.9
1–4	8.6	6–8	9.8	15–16	2.0		
1–5	12.9	9–10	40.0	17–18	8.4		
1–6	30.6	1–9	12.9	1–10	27.4		

α-form crystallizes first from cooling reaction solutions suggesting that its formation is kinetically controlled. It would seem that the hydrogen-bonding requirements are major determinants of crystal form and the differences in molecular structure again reflect the ability of bivalent copper to adopt intermediate geometries.

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