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Studies on the Metal–Amide Bond. XI*. The Structure of Aqua[N,N′-bis(2′-pyridinecarboxamido)-*trans*-1,2-cyclohexane]copper(II) Dihydrate

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*Aqua[N,N′-bis(2′-pyridinecarboxamido)-*trans*-1,2-cyclohexane]copper(II) dihydrate, $C_{18}H_{24}N_4O_5Cu$, is monoclinic, space group P2$_1$/c, with a = 9.094(10), b = 17.620(7), c = 12.141(7) Å, β = 91.9(1)°, Z = 4. The structure was refined to R = 0.088 for 2787 photographic reflexions using least-squares calculations. The copper atom is five-coordinate with the ligand acting as an essentially planar N_4-tetradentate which encompasses the base of a distorted square-based pyramid [average Cu–N(*amide*) 1.934(5), Cu–N(*pyridine*) 2.026(5) Å, N(*amide*)–Cu–N(*amide*) 83.5(2)°, N(*pyridine*)–Cu–N(*pyridine*) 110.2(1)°]. The copper atom is displaced by 0.19 Å from the N_4-plane towards the apical water molecule [Cu–O 2.338(5) Å]. Both amide nitrogen atoms are approximately 50% pyramidally distorted. The cyclohexane ring adopts a chair conformation in which the two methine hydrogen atoms are in a* trans *configuration. The coordinated and the two lattice water molecules are involved in a hydrogen-bond network which includes the carboxyl oxygen atoms of the amide groups of neighbouring chelate molecules. The chelate molecules pack in layers parallel to (101).*

Introduction

Three crystalline forms of the deprotonated copper(II) complex of N,N′-bis(2′-pyridinecarboxamide)-1,2-cyclohexane, bpchH$_2$, have been isolated [1]. The crystal structures of two of these forms, [Cu(*trans*-bpch)H$_2$O]H$_2$O [1] and [Cu(*cis*-bpch)-H$_2$O]H$_2$O [2], have been reported. In both structures the copper atom has a distorted square-pyramidal environment in which the N$_4$-ligand encompasses the base and a water molecule occupies the apical site. We here report the crystal structure of the third form, [Cu(*trans*-bpch)H$_2$O]2H$_2$O.

Experimental

Crystal Data

$C_{18}H_{24}N_4O_5Cu$, M_r = 439.9, Monoclinic, a = 9.094(10), b = 17.620(7), c = 12.141(7) Å, β = 91.9(1)°, U = 1944.4 Å^3, Z = 4, D_c = 1.503 Mg m^{-3}, F(000) = 916, μ(Cu-K_α) = 2.06 mm^{-1}, μ(Mo-K_α) = 1.19 mm^{-1}. Systematic absences: $h0l$ if $l \neq 2n$ and $0k0$ if $k \neq 2n$, space group $P2_1/c$ (No. 14).

The complex crystallises as blue–violet [001] elongated octahedra with [010] directed through an apex. Cell parameters were determined from precession photographs using Mo-K_α radiation. Intensities were estimated visually from equi-inclination Weissenberg photographs for the layers 0–5kl and hk0–5 using Cu-K_α radiation and from precession photographs for the layers h0–3l using Mo-K_α radiation. They were corrected for Lorentz and polarisation effects but not for extinction or absorption. The observed structure factors were placed on a common scale by internal correlation and 2787 non-zero unique reflexions were obtained. Scattering factors were taken from 'International Tables for X-Ray Crystallography' [3] and all calculations were carried out on a UNIVAC 1106 computer with programmes written by F.S.S..

Structure Determination

The structure was solved by the heavy atom method. Refinement was carried out by full-matrix least-squares calculations in which $\Sigma w\Delta^2$ was minimised. The weight, w, for each reflexion was initially unity and in the final cycles given by $w = (15.0 + |F_o| + 0.05\,|F_o|^2)^{-1}$. Reflexions, for which $|F_c| < 0.1\,|F_o|$, were omitted from the least-squares analysis. After isotropic refinement, a difference map yielded the approximate positions of the hydrogen atoms. Their positions were optimised, assuming C–H and O–H to be 1.0 and 0.9 Å respectively, and they were included in subsequent calculations but their parameters were not refined. The anisotropic refinement for all non-hydrogen atoms was terminated when the

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*Part X. R. L. Chapman, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 52,* 169 (1981).

maximum shift in any parameter was $<0.1\sigma$. In the final cycle 2781 reflexions were included. The final value for R, based on 2787 reflexions, was 0.088 and for $R' [=(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}]$ was 0.130. A final difference map showed no positive density >0.8 eÅ^{-3}. The final atomic parameters are given in Tables I, II and III. A list of observed and calculated structure factors has been deposited with the Editor.

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

	x	y	z
Cu	2341.7(10)	1218.2(5)	481.1(7)
O(W1)	233(6)	1424(3)	−633(4)
O(1)	524(6)	2734(3)	2437(5)
O(2)	5927(6)	1575(3)	−1226(4)
N(11)	1253(7)	795(3)	1775(5)
N(21)	3015(6)	363(3)	−496(4)
N(1)	2210(7)	2147(3)	1322(5)
N(2)	3747(7)	1788(3)	−345(5)
C(1)	2717(8)	2802(3)	720(6)
C(2)	4059(8)	2552(4)	104(5)
C(3)	4429(10)	3148(4)	−770(6)
C(4)	4753(14)	3914(5)	−157(9)
C(5)	3494(11)	4149(4)	553(8)
C(6)	3098(10)	3522(4)	1371(7)
C(11)	720(9)	1376(4)	2392(5)
C(12)	−131(11)	1255(5)	3294(7)
C(13)	−400(12)	520(6)	3610(8)
C(14)	131(11)	−76(5)	3019(7)
C(15)	950(11)	75(4)	2095(7)
C(21)	4185(8)	578(3)	−1070(5)
C(22)	4881(10)	91(4)	−1759(6)
C(23)	4349(11)	−658(4)	−1865(7)
C(24)	3148(11)	−860(4)	−1325(7)
C(25)	2491(9)	−349(4)	−642(6)
C(01)	1165(9)	2165(4)	3032(5)
C(02)	4704(8)	1390(4)	−884(5)
O(W2)	−1900(6)	2448(4)	−111(5)
O(W3)	−2432(10)	3020(8)	1942(7)

Discussion

The bond lengths and angles are given in Table IV. Figure 1 shows a perspective drawing [4] of the chelate molecule together with the atom labelling. The molecular packing and the hydrogen-bonding in the cell are shown in Fig. 2. Table V lists the proposed donor-acceptor hydrogen bond distances and other intermolecular contacts <3.5 Å. The hydrogen-bond network involves both the coordinated and the lattice water molecules together with the carboxyl oxygen atoms of the amide groups of the ligand. Each carboxyl oxygen atom acts as an acceptor in two hydrogen bonds. This contrasts with the situation in the structures of [Cu(*trans*-bpch)H_2O]H_2O [1], [Cu(*cis*-bpch)H_2O]H_2O [2] and [Cu(bpen)H_2O]H_2O [5] in which only three hydrogen bonds form to the carboxyl oxygen atoms. Further, the chelate molecules in the latter structures pack in layers parallel to (10$\bar{1}$) whereas in the present structure they are parallel to (101).

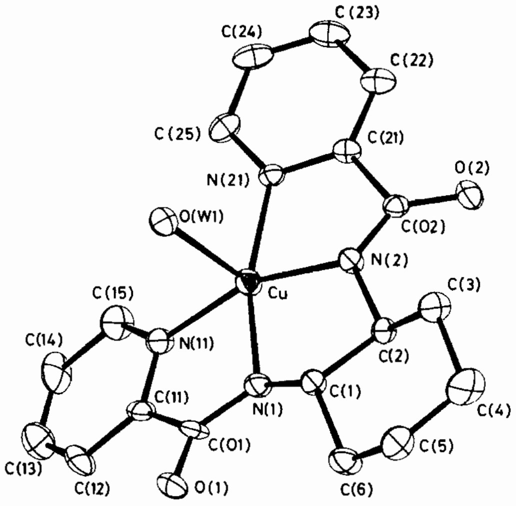

Fig. 1. A perspective drawing of the chelate molecule with the atom labelling. Thermal ellipsoids are drawn to include 35% probability.

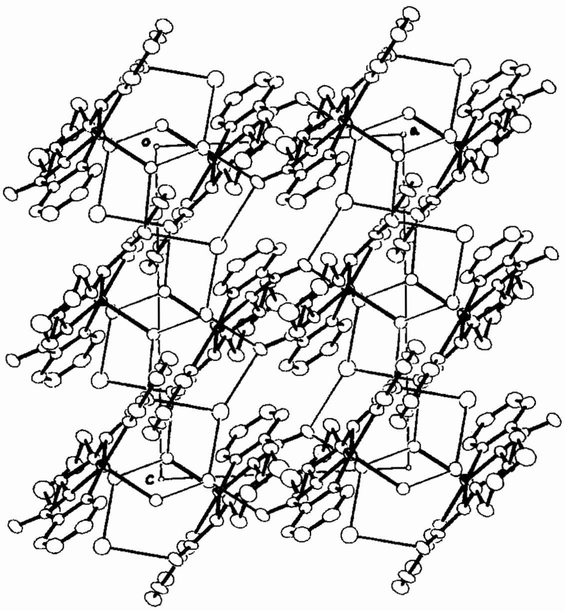

Fig. 2. The packing of the molecules in the unit cell. The hydrogen bonds are represented by thin lines.

The copper atom is five-coordinate with the ligand acting as a tetradentate. The four nitrogen donor atoms lie at the corners of the base of a distorted square-pyramid and with a water molecule [Cu–O-

TABLE II. 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	85(1)	18.1(3)	44.6(7)	–4.0(5)	17.4(7)	–1.5(3)
O(W1)	82(7)	22(1)	43(3)	2(3)	5(4)	4(2)
O(1)	105(8)	28(2)	55(4)	–2(3)	30(5)	–15(2)
O(2)	96(7)	28(2)	52(4)	–9(3)	28(4)	–4(2)
N(11)	104(9)	18(2)	36(4)	–12(3)	12(5)	1(2)
N(21)	72(7)	14(1)	35(3)	–2(3)	3(4)	–5(2)
N(1)	88(8)	15(1)	43(4)	–4(3)	13(5)	–5(2)
N(2)	76(7)	13(1)	40(4)	–1(3)	14(4)	0(2)
C(1)	79(9)	13(2)	44(4)	–3(3)	13(5)	–1(2)
C(2)	84(9)	15(2)	35(4)	–12(3)	11(5)	3(2)
C(3)	137(12)	18(2)	44(5)	–15(4)	9(7)	6(3)
C(4)	218(20)	19(2)	93(8)	–37(6)	25(11)	0(4)
C(5)	146(13)	14(2)	84(7)	–17(4)	23(8)	–4(3)
C(6)	135(12)	17(2)	57(5)	–4(4)	27(7)	–9(3)
C(11)	95(10)	22(2)	24(4)	–7(4)	3(5)	–4(2)
C(12)	141(13)	38(3)	43(5)	–20(5)	45(7)	–2(3)
C(13)	143(14)	45(4)	59(6)	–15(6)	29(8)	7(4)
C(14)	126(13)	38(3)	61(6)	–20(6)	16(8)	26(4)
C(15)	158(14)	21(2)	59(6)	–21(5)	22(8)	9(3)
C(21)	74(8)	13(2)	36(4)	8(3)	–2(5)	–1(2)
C(22)	111(11)	23(2)	41(5)	13(4)	–7(6)	–5(3)
C(23)	156(14)	21(2)	64(6)	19(5)	9(8)	–14(3)
C(24)	164(14)	16(2)	51(5)	4(4)	–17(7)	–8(3)
C(25)	100(11)	17(2)	52(5)	–5(4)	–14(6)	2(2)
C(01)	105(10)	19(2)	24(4)	2(4)	16(5)	–7(2)
C(02)	71(8)	18(2)	28(4)	–1(3)	–1(5)	0(2)
O(W2)	85(7)	39(2)	62(4)	–4(3)	10(5)	–7(3)
O(W3)	142(12)	154(9)	81(6)	60(9)	1(7)	–50(6)

TABLE III. Atomic Parameters for Hydrogen Atoms (coordinates: fractional, $\times 10^3$).[a]

	x	*y*	*z*
H(1)	206	294	6
H(2)	497	258	59
H(31)	361	324	–133
H(32)	538	298	–108
H(41)	495	434	–67
H(42)	565	380	32
H(51)	382	461	97
H(52)	258	428	11
H(61)	226	368	180
H(62)	396	342	187
H(12)	–54	169	371
H(13)	–99	42	428
H(14)	–6	–61	325
H(15)	132	–36	165
H(22)	575	26	–218
H(23)	486	–103	–234
H(24)	273	–138	–142
H(25)	160	–51	–24
H(W11)	29	168	–127
H(W12)	–46	176	–44
H(W21)	–264	226	–53
H(W22)	–209	277	44
H(W31)	–148	288	212
H(W32)	–299	319	248

[a] For all hydrogen atoms $B = 6.0$ Å^2.

(W1) 2.338(5) Å] occupying the apical site. The copper atom is raised by 0.19 Å above the N$_4$-plane (Table VI, plane 1) towards the water molecule. The square-based pyramid is slightly distorted towards trigonal bipyramidal geometry as evidenced by the dihedral angles of 101, 95 and 7° between the relevant three donor-atom planes (Table VI, planes 7–9). The Cu–O(W1) bond 'leans' 3° from the normal to the N$_4$-plane towards the open side of the ligand and this value is considerably less than that of 8.7 and 13.6° found in the related monohydrate [1] and the *cis*-isomer [2] respectively. The average Cu–N(*amide*) and Cu–N(*pyridine*) distances of 1.934(5) and 2.026(5) Å respectively are comparable with those in analogous complexes [1, 2, 5, 6].

Both amide chelate rings (Table VI, planes 4 and 5) show significant distortions from planarity and the

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

a) *Distances* (Å)

Cu–O(W1)		2.338(5)	
		$n = 1$	$n = 2$
Cu–N(n1)		2.026(5)	2.025(5)
Cu–N(n)		1.935(5)	1.932(6)
N(n1)–C(n5)		1.357(9)	1.352(8)
C(n5)–C(n4)		1.393(11)	1.374(11)
C(n4)–C(n3)		1.369(14)	1.340(13)
C(n3)–C(n2)		1.375(13)	1.411(11)
C(n2)–C(n1)		1.378(10)	1.368(10)
C(n1)–N(n1)		1.368(9)	1.345(9)
C(n1)–C(On)		1.515(9)	1.522(8)
C(On)–O(n)		1.268(8)	1.244(9)
C(On)–N(n)		1.305(9)	1.310(9)
N(n)–C(n)		1.450(8)	1.476(8)
C(1)–C(2)	1.518(10)	C(5)–C(4)	1.513(14)
C(1)–C(6)	1.528(9)	C(2)–C(3)	1.539(9)
C(6)–C(5)	1.537(11)	C(3)–C(4)	1.564(11)

b) *Angles* (°)

N(1)–Cu–N(21)	164.5(2)	N(2)–Cu–N(11)	160.4(2)
N(1)–Cu–N(2)	83.5(2)	N(11)–Cu–N(21)	110.2(1)
		$n = 1$	$n = 2$
N(n)–Cu–N(n1)		82.1(1)	82.2(2)
N(n1)–Cu–O(W1)		95.3(2)	92.0(2)
N(n)–Cu–O(W1)		96.3(2)	99.4(2)
C(n5)–N(n1)–Cu		132.5(5)	130.9(4)
C(n1)–N(n1)–Cu		109.9(4)	110.8(5)
C(n5)–N(n1)–C(n1)		117.6(6)	118.3(6)
C(On)–N(n)–Cu		115.3(5)	116.3(4)
C(n)–N(n)–Cu		112.5(4)	113.9(4)
C(n)–N(n)–C(On)		124.4(6)	123.4(6)
C(n1)–C(On)–N(n)		112.1(6)	111.7(6)
C(n1)–C(On)–O(n)		118.9(7)	118.2(6)
O(n)–C(On)–N(n)		129.0(6)	130.0(6)
C(n2)–C(n1)–N(n1)		122.6(7)	122.1(5)
C(n2)–C(n1)–C(On)		122.2(6)	122.2(6)
N(n1)–C(n1)–C(On)		115.2(7)	115.7(7)
C(n3)–C(n2)–C(n1)		118.5(8)	118.6(8)
C(n4)–C(n3)–C(n2)		120.5(8)	119.1(7)
C(n5)–C(n4)–C(n3)		118.8(8)	120.0(7)
N(n1)–C(n5)–C(n4)		121.9(8)	121.9(7)
N(1)–C(1)–C(2)	106.9(5)	N(2)–C(2)–C(1)	114.3(5)
N(1)–C(1)–C(6)	118.1(6)	N(2)–C(2)–C(3)	107.4(5)
C(6)–C(1)–C(2)	108.9(6)	C(3)–C(2)–C(1)	109.8(6)
C(2)–C(3)–C(4)	107.6(6)	C(1)–C(6)–C(5)	108.4(6)
C(3)–C(4)–C(5)	111.9(8)	C(6)–C(5)–C(4)	111.7(7)

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

a) Proposed donor-acceptor hydrogen bond distances[a]

O(W1)–H(W11)····O(1^{I})	2.793(7)
O(W1)–H(W12)····O(W2)	2.739(8)
O(W2)–H(W21)····O(2^{II})	2.816(8)
O(W2)–H(W22)····O(W3)	2.746(10)
O(W3)–H(W31)····O(1)	2.781(10)
O(W3)–H(W32)····O(2^{III})	2.812(10)

b) Intermolecular distances <3.5 Å[a]

O(W1)····C(15^{IV})	3.341(9)
N(21)····C(22^{V})	3.384(10)
C(02)····C(24^{V})	3.397(10)
C(25)····O(2^{V})	3.415(9)
C(24)····O(2^{V})	3.423(10)
C(12)····O($W2^{VI}$)	3.431(11)

[a] Roman numeral superscripts refer to the following equivalent positions relative to x, y, z:

I	$x, \frac{1}{2} - y, z - \frac{1}{2}$	IV	$-x, -y, -z$
II	$x - 1, y, z$	V	$1 - x, -y, -z$
III	$x-1, \frac{1}{2} - y, \frac{1}{2} + z$	VI	$x, \frac{1}{2} - y, \frac{1}{2} + z$

copper atom is displaced from each plane by 0.45 and 0.53 Å respectively. The dihedral angle between the planes of these chelate rings and the respective pyridine ring planes is 10.2 and 6.3°. The third chelate ring which contains the ethylene link is necessarily non-planar (Table VI, plane 6) and its plane has a dihedral angle of 8.3° with the N_4-plane. The two planar pyridine rings (Table VI, planes 2 and 3) have a dihedral angle between their planes of 24.7° which is approximately the result of their rotations of 11.7 and 17.4°, respectively, in opposite directions relative to the N_4-plane. Such rotations give rise to a separation of 2.37 Å between the two hydrogen atoms in the 6-positions of these rings. This arrangement, as a whole, closely resembles that found for the second molecule in the structure of [Cu(bpen)H_2O]·H_2O [5] and markedly contrasts with the folding of the picolinamide moieties in the related monohydrate structure [1].

Both amide nitrogen atoms show a large deviation from planarity towards a pyramidal geometry. The distortion, as measured by the average of the dihedral angles between the relevant three atom planes (Table VI, planes 13–18), is 31.7° for N(1) and 28.8° for N(2) and is comparable with that of 30.8° in the square-planar [Ni(*trans*-bpch)] structure [7]. The reason that the distortion is considerably more than that of 14.5 and 10.0° found in the related monohydrate structure [1] is not readily evident. Both carboxyl carbon atoms have the expected trigonal-planar arrangement (Table VI, planes 19–24).

TABLE VI. Least-Squares Planes Data.

a) Least-squares planes and their equations given by $lX' + mY' + nZ' - p = 0$ where X', Y' and Z' are orthogonal coordinates (Å) derived with respect to the orthogonal axes a', b, c. Deviations (Å) of relevant atoms from the planes are given in square brackets.

	l	*m*	*n*	*p*
Plane (1): N(11), N(21), N(1), N(2) [N(11) 0.047; N(21) –0.047; N(1) –0.061; N(2) 0.061; Cu –0.19; O(W1) –2.52]	0.8088	–0.2068	0.5505	1.7498
Plane (2): N(11), C(11) –C(15) [N(11) –0.002; C(11) 0.012; C(12) –0.013; C(13) 0.004; C(14) 0.006; C(15) –0.007; Cu –0.06; C(01) 0.10]	0.8339	–0.0041	0.5519	2.1140
Plane (3): N(21), C(21) –C(25) [N(21) 0.017; C(21) –0.008; C(22) –0.009; C(23) 0.018; C(24) –0.010; C(25) –0.008; Cu 0.09; C(02) <|0.01|]	0.5963	–0.3028	0.7435	0.9085
Plane (4): N(11), C(11), C(01), N(1) [N(11) –0.032; C(11) 0.056; C(01) –0.057; N(1) 0.033; Cu –0.45; O(1) –0.21]	0.7310	–0.0747	0.6783	2.1961
Plane (5): N(21), C(21), C(02), N(2) [N(21) 0.032; C(21) –0.054; C(02) 0.054; N(2) –0.032; Cu 0.33; O(2) 0.23]	0.5514	–0.2232	0.8038	0.7794
Plane (6): N(1), C(1), C(2), N(2) [N(1) 0.13; C(1) –0.22; C(2) 0.22; N(2) –0.12; Cu –0.20; C(01) 0.02; C(02) 0.17]	0.7303	–0.1631	0.6634	1.7445
Plane (7): N(1), N(21), O(W1) [Cu –0.20]	0.4536	0.5837	–0.6735	2.0835
Plane (8): N(1), N(21), N(11) [Cu –0.15]	0.8336	–0.1773	0.5231	1.8085
Plane (9): N(1), N(21), N(2) [Cu –0.12]	0.7683	–0.2418	0.5926	1.5402
Plane (10): C(1), C(2), C(4), C(5) [C(1), C(4) –0.034; C(2), C(5) 0.034; C(3) –0.72; C(6) 0.73]	0.5653	–0.0610	0.8226	1.7806
Plane (11): C(3), C(2), C(4)	0.9674	–0.2456	0.0624	2.4645
Plane (12): C(6), C(1), C(5)	0.9587	–0.2823	0.0337	1.0005
Plane (13): N(1), Cu, C(1) [C(01) –0.58]	0.9272	–0.1477	0.3441	1.8331
Plane (14): N(1), Cu, C(01) [C(1) –0.66]	0.6277	–0.3796	0.6796	0.8702
Plane (15): N(1), C(1), C(01) [Cu –0.96]	0.6764	0.1897	0.7117	3.1710
Plane (16): N(2), Cu, C(2) [C(02) 0.54]	0.7455	–0.3759	0.5503	1.0625
Plane (17): N(2), Cu, C(02) [C(2) 0.62]	0.6259	0.0151	0.7798	1.7649
Plane (18): N(2), C(2), C(02) [Cu –0.86]	–0.3377	0.4086	–0.8479	0.5874
Plane (19): C(01), C(11), O(1) [N(1) 0.01]	0.6902	0.0329	0.7229	2.6149
Plane (20): C(01), C(11), N(1) [O(1) 0.01]	0.6858	0.0355	0.7270	2.6300
Plane (21): C(01), O(1), N(1) [C(11) 0.01]	0.6858	0.0282	0.7272	2.6028

TABLE VI. (*Continued*)

Plane (22): C(02), C(21), O(2) [N(2) 0.03]	0.4288	−0.2674	0.8629	0.1294
Plane (23): C(02), C(21), N(2) [O(2) 0.03]	0.4496	−0.2725	0.8506	0.2208
Plane (24): C(02), O(2), N(2) [C(21) 0.04]	0.4325	−0.2951	0.8520	0.0906

b) Dihedral angles (°) between relevant planes

1–2	11.7	7–8	94.5
1–3	17.4	7–9	101.1
1–6	8.3	8–9	6.6
2–3	24.5	10–11	52.2
2–4	10.2	10–12	54.1
3–5	6.3	11–12	2.7
13–14	29.3	19–20	0.4
13–15	32.4	19–21	0.4
14–15	33.3	20–21	0.4
16–17	27.1	22–23	1.4
16–18	150.7(29.3)	22–24	1.7
17–18	150.1(29.9)	23–24	1.6

The cyclohexane ring adopts a chair conformation with the two methine hydrogen atoms in a *trans* configuration. The two three atom planes (Table VI, planes 11 and 12) have an average dihedral angle of 53° with the plane of the 'seat' of the chair (Table VI, plane 10) which is close to the value of 54.7° for an ideal chair conformation and contrasts with that of 33° for the skew-chair conformation in the related monohydrate structure [1].

There are clearly significant differences in the structures of the [Cu(*trans*-bpch)H_2O] molecule in its two lattice hydrate forms. The origin of these differences is not readily obvious. However, it is evident that in order to obtain essentially N_4-planar coordination distortion at the amide nitrogen atoms and/or within the cyclohexane ring must occur. The degree of such competing distortions relative to one another would appear to be largely influenced by the hydrogen bonding requirements in the solid state.

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