Inorganica Chimica Acta, 51 (1981) 149–154

Studies on the Metal–Amide Bond. VI*. The Crystal Structure of Aqua[N,N'-bis(2'-pyridinecarboxamido)-*cis*-1,2-cyclohexane]copper(II) Monohydrate

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Received March 4, 1981

*Aqua[N,N'-bis(2'-pyridinecarboxamido)-*cis*-1,2-cyclohexane]copper(II) monohydrate, $C_{18}H_{22}N_4O_4$-Cu, is monoclinic, space group C2/c, with* a = *19.985(8),* b = *11.114(3),* c = *17.581(5) Å, β = 112.5(1)°, Z = 8. The structure was refined to* R = *0.082 for 2224 photographic reflexions by full-matrix least-squares calculations. The copper atom is five-coordinate with the N_4-tetradentate ligand encompassing the base of a distorted square-based pyramid [average Cu–N(*amide*) 1.933(8); Cu–N (*pyridine*)* 2.027(7) Å, *N(*amide*)–Cu–N(*amide*) 83.2(3)°, N(*pyridine*)–Cu–N(*pyridine*) 111.0(3)°] and with the Cu atom lying 0.19 Å above the N_4 plane towards the apical water molecule [Cu–O 2.382(7) Å]. Both amide nitrogen atoms show approximately 35% pyramidal distortion. The cyclohexane ring adopts a chair conformation with the two methine hydrogen atoms in a *cis*-conformation. The molecules pack in sheets parallel to (10$\bar{1}$) and a hydrogen-bond network involves both water molecules and the amide oxygen atoms of the ligand.*

Introduction

Recently we reported the synthesis and characterisation of some metal complexes of the potentially tetradentate bis-amide ligand N,N'-bis(2'-pyridinecarboxamide)-1,2-cyclohexane (bpchH_2) [1]. The ligand as prepared was a mixture of both *cis*- and *trans*-isomers of the cyclohexane fragment. For the deprotonated copper(II) complexes three solid forms that co-crystallise have been identified and the crystal structure of one of these derived from the *trans*-isomer of the ligand, [Cu(*trans*-bpch)H_2O]H_2O, has been reported [2]. We report now the structure analysis of the second form, [Cu(*cis*-bpch)H_2O]H_2O.

Experimental

Crystal Data

$C_{18}H_{22}N_4O_4Cu$, M_r = 421.9, Monoclinic, a = 19.985(8), b = 11.114(3), c = 17.581(5) Å, β = 112.5(1)°, U = 3607.7 Å^3, Z = 8, D_c = 1.553 Mg m^{-3}, $F(000)$ = 1752, $\mu(\text{Mo}-K_\alpha)$ = 1.29 mm^{-1}. Systematic absences hkl if $h + k \neq 2n$ and $h0l$ if $l \neq 2n$, space group Cc (No. 9) or $C2/c$ (No. 15).

The complex crystallises as blue–violet diamond-shaped plates elongated along [001] and lying on (100), a like form to the *trans*-isomer, [Cu(*trans*-bpch)H_2O]H_2O [2]. Cell parameters were determined from precession photographs using Mo–K_α radiation. Intensities were estimated visually from precession photographs for the layers h0–3l and hk0–5. They were corrected for Lorentz and polarisation effects but not for absorption or extinction. The structure factors were placed on a common scale by internal correlation and 2224 non-zero unique reflexions were obtained. Scattering factors were taken from *International Tables for X-ray Crystallography* [3]. All calculations were carried out on a UNIVAC 1106 computer with programmes written by F.S.S.

Structure Determination

A three-dimensional Patterson synthesis indicated the space group to be centric. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures in which $\Sigma w\Delta^2$ was minimised. Weights for each reflexion, w, were initially unity and in the final stages given by $w = (20.0 + 0.5|F_o| + 0.02|F_o|^2)^{-1}$. Hydrogen atom positions were calculated assuming the appropriate geometries for the carbon and oxygen atoms with O–H 0.9 Å and C–H 1.0 Å. The contribution of these atoms was included in the calculations but their parameters were not refined. Refinement was terminated when the maximum shift in any parameter was <0.01σ. The final R was 0.082 and R' [$=(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}$]

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*Part V is reference [2].

TABLE I. Final Atomic Co-ordinates (fractional × 10^4) with Estimated Standard Deviations in Parentheses.

	x/a	y/b	z/c
Cu	2241.5(5)	573.6(9)	990.8(6)
O(W1)	1736(4)	645(7)	2016(5)
N(11)	2015(4)	2331(7)	773(4)
N(21)	3226(3)	332(7)	1930(5)
N(2)	2338(3)	−1139(7)	900(5)
N(1)	1482(4)	394(6)	−94(5)
C(11)	1517(4)	2501(7)	9(5)
C(12)	1304(5)	3633(9)	−298(6)
C(13)	1594(5)	4616(8)	30(8)
C(14)	2077(5)	4467(9)	998(7)
C(15)	2280(4)	3298(9)	1248(6)
C(01)	1233(4)	1401(7)	−505(5)
C(1)	1438(4)	−818(8)	−445(6)
C(2)	1705(4)	−1685(7)	279(6)
C(3)	1134(5)	−1924(9)	648(6)
C(4)	410(6)	−2304(12)	5(8)
C(5)	139(5)	−1368(11)	−695(7)
C(6)	689(6)	−1231(10)	−1084(6)
C(02)	2808(4)	−1701(8)	1518(5)
C(21)	3361(4)	−865(7)	2090(5)
C(22)	3992(5)	−1234(10)	2696(6)
C(23)	4477(5)	−396(13)	3171(7)
C(24)	4344(5)	799(10)	3023(7)
C(25)	3701(5)	1138(9)	2401(6)
O(1)	805(4)	1547(6)	−1246(4)
O(2)	2837(4)	−2805(6)	1674(5)
O(W2)	742(4)	−979(8)	2216(4)

TABLE III. Hydrogen Atom Parameters (co-ordinates: fractional × 10^3).[a]

	x/a	y/b	z/c
H(12)	94	374	−87
H(13)	145	544	−2
H(14)	228	517	138
H(15)	265	317	182
H(22)	410	−211	279
H(23)	493	−67	363
H(24)	470	141	335
H(25)	359	202	230
H(1)	181	−87	−72
H(2)	187	−244	7
H(31)	132	−261	108
H(32)	104	−123	96
H(41)	47	−311	−24
H(42)	4	−241	26
H(51)	7	−59	−46
H(52)	−33	−165	−113
H(61)	49	−66	−155
H(62)	73	−206	−132
H(W11)	187	116	246
H(W12)	141	12	209
H(W21)	27	−115	193
H(W22)	76	−117	273

[a] For all H atoms $B = 6.0$ Å^2.

TABLE II. Final Anisotropic Thermal Parameters (×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	20.4(3)	33.6(7)	21.6(4)	−0.8(4)	−0.9(2)	−0.3(8)
O(W1)	35(2)	91(7)	38(3)	−15(3)	19(2)	−15(6)
N(11)	22(2)	49(6)	21(2)	−5(3)	3(2)	0(5)
N(21)	18(2)	60(6)	27(3)	−2(3)	9(2)	−3(6)
N(2)	23(2)	46(5)	29(3)	−3(3)	9(2)	−6(6)
N(1)	24(2)	39(5)	18(2)	−5(2)	1(2)	−1(5)
C(11)	20(2)	39(5)	16(2)	−3(3)	4(2)	1(6)
C(12)	24(2)	59(7)	33(4)	3(3)	7(3)	−5(7)
C(13)	30(3)	37(6)	48(5)	−1(3)	12(3)	8(7)
C(14)	29(3)	51(7)	43(5)	4(4)	9(3)	−6(8)
C(15)	23(2)	57(6)	25(3)	−5(3)	4(2)	−16(7)
C(01)	19(2)	44(6)	21(3)	−2(3)	4(2)	−6(6)
C(1)	23(2)	49(6)	26(3)	−4(3)	3(2)	−14(7)
C(2)	22(2)	35(5)	27(3)	−1(3)	7(2)	−4(6)
C(3)	27(2)	75(8)	29(3)	−15(4)	12(3)	−16(7)
C(4)	30(3)	108(12)	55(6)	−24(5)	19(4)	−30(10)
C(5)	21(2)	98(11)	49(5)	−2(4)	−5(3)	−31(9)
C(6)	36(3)	71(9)	28(3)	−7(4)	0(3)	−3(8)
C(02)	25(2)	45(6)	19(3)	3(3)	6(2)	11(7)
C(21)	19(2)	45(5)	25(3)	7(3)	6(2)	4(7)

(continued on facing page)

TABLE II. *(continued)*

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(22)	25(3)	85(9)	32(4)	11(4)	0(3)	4(8)
C(23)	25(3)	127(14)	38(4)	8(5)	−9(3)	3(11)
C(24)	20(2)	77(9)	35(4)	−2(3)	−4(2)	11(8)
C(25)	24(2)	58(7)	35(4)	−7(4)	1(2)	−4(7)
O(1)	26(2)	38(5)	11(2)	0(3)	−1(2)	3(5)
O(2)	30(2)	28(4)	20(3)	2(3)	4(2)	11(5)
O(W2)	24(2)	87(8)	23(2)	−4(3)	11(2)	8(6)

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

Distances (A)			
	Cu–O(W1)	2.382(7)	
Cu–N(11)	2.009(7)	Cu–N(21)	2.045(7)
Cu–N(1)	1.925(8)	Cu–N(2)	1.941(7)
N(11)–C(11)	1.344(10)	N(21)–C(21)	1.365(11)
N(11)–C(15)	1.340(11)	N(21)–C(25)	1.334(11)
N(1)–C(01)	1.323(10)	N(2)–C(02)	1.293(11)
N(1)–C(1)	1.469(10)	N(2)–C(2)	1.451(10)
C(01)–O(1)	1.265(9)	C(02)–O(2)	1.254(10)
C(11)–C(12)	1.371(12)	C(21)–C(22)	1.365(11)
C(12)–C(13)	1.380(13)	C(22)–C(23)	1.374(16)
C(13)–C(14)	1.376(15)	C(23)–C(24)	1.359(17)
C(14)–C(15)	1.382(13)	C(24)–C(25)	1.384(12)
C(11)–C(01)	1.497(11)	C(21)–C(02)	1.499(11)
C(1)–C(2)	1.520(13)	C(4)–C(5)	1.543(18)
C(2)–C(3)	1.537(13)	C(5)–C(6)	1.508(16)
C(3)–C(4)	1.515(13)	C(6)–C(1)	1.558(12)
Angles (°)			
O(W1)–Cu–N(11)	89.0(3)	O(W1)–Cu–N(21)	87.1(3)
O(W1)–Cu–N(1)	110.4(3)	O(W1)–Cu–N(2)	100.4(3)
N(11)–Cu–N(1)	83.0(3)	N(21)–Cu–N(2)	80.9(3)
N(11)–Cu–N(21)	111.0(3)	N(2)–Cu–N(1)	83.2(3)
N(11)–Cu–N(2)	165.4(3)	N(21)–Cu–N(1)	158.3(3)
Cu–N(11)–C(11)	110.7(5)	Cu–N(21)–C(21)	110.4(5)
Cu–N(11)–C(15)	130.9(6)	Cu–N(21)–C(25)	130.4(6)
C(11)–N(11)–C(15)	118.4(8)	C(21)–N(21)–C(25)	119.2(7)
Cu–N(1)–C(01)	116.1(5)	Cu–N(2)–C(02)	118.1(6)
Cu–N(1)–C(1)	113.9(5)	Cu–N(2)–C(2)	113.0(5)
C(01)–N(1)–C(1)	126.7(7)	C(02)–N(2)–C(2)	125.0(8)
C(11)–C(01)–O(1)	117.9(8)	C(21)–C(02)–O(2)	119.9(7)
N(1)–C(01)–O(1)	129.5(8)	N(2)–C(02)–O(2)	127.9(8)
C(11)–C(01)–N(1)	112.6(7)	C(21)–C(02)–N(2)	112.1(8)
C(01)–C(11)–N(11)	117.0(7)	C(02)–C(21)–N(21)	115.4(7)
C(01)–C(11)–C(12)	121.5(7)	C(02)–C(21)–C(22)	124.2(8)
N(11)–C(11)–C(12)	121.4(8)	N(21)–C(21)–C(22)	120.3(8)
C(11)–C(12)–C(13)	119.1(8)	C(21)–C(22)–C(23)	119.8(10)
C(12)–C(13)–C(14)	120.7(8)	C(22)–C(23)–C(24)	120.4(9)
C(13)–C(14)–C(15)	116.4(9)	C(23)–C(24)–C(25)	118.2(9)
C(14)–C(15)–N(11)	123.9(8)	C(24)–C(25)–N(21)	122.1(9)
N(1)–C(1)–C(2)	106.5(7)	N(2)–C(2)–C(1)	106.9(7)
N(1)–C(1)–C(6)	117.3(7)	N(2)–C(2)–C(3)	109.2(7)
C(6)–C(1)–C(2)	110.4(7)	C(3)–C(2)–C(1)	112.6(7)
C(5)–C(6)–C(1)	111.7(8)	C(4)–C(3)–C(2)	112.5(8)
C(6)–C(5)–C(4)	109.5(8)	C(5)–C(4)–C(3)	110.6(9)

TABLE V. Contact Distances (Å).[a]

Hydrogen Bonds in Donor-Acceptor Distances	
$O(W2)-H(W22)\cdots\cdots O(1^{I})$	2.73
$O(W1)-H(W11)\cdots\cdots O(2^{II})$	2.74
$O(W1)-H(W12)\cdots\cdots O(W2)$	2.80
$O(W2)-H(W21)\cdots\cdots O(1^{III})$	2.97

Intermolecular Distances < 3.5 Å			
$C(3)\cdots\cdots O(W2)$	3.31	$C(14)\cdots\cdots O(2^{V})$	3.40
$C(25)\cdots\cdots O(W2^{II})$	3.38	$O(W2)\cdots\cdots O(W2^{VI})$	3.47
$C(1)\cdots\cdots O(2^{IV})$	3.39		

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

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

was 0.114. A final difference map showed no features $>|1.1|\,e\text{Å}^{-3}$ and these were associated with the copper atom. The final atomic parameters are given in Tables I–III. A list of observed and calculated structure factors has been deposited with the Editor.

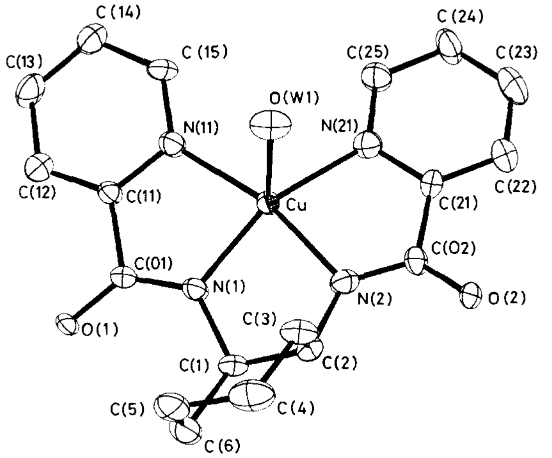

Fig. 1. A perspective drawing of the chelate molecule [4] with the labelling of the atoms. Thermal ellipsoids are drawn to include 35% probability.

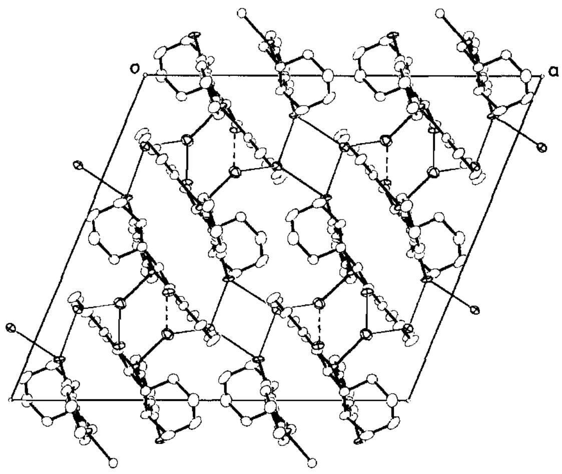

Fig. 2. The molecular packing in the unit cell. The hydrogen bonds are represented by thin and broken lines, the latter indicating that one of the atoms involved is a *b*-cell translation away from that represented.

Discussion

The bond lengths and angles are given in Table IV. Figure 1 gives a perspective drawing of the chelate molecule [4] and the labelling of the atoms. The molecular packing and the hydrogen-bonding in the unit cell are shown in Fig. 2. The donor-acceptor hydrogen-bond distances and intermolecular contacts <3.5 Å are given in Table V. The chelate molecules pack in sheets parallel to $(10\bar{1})$. The hydrogen-bond network and the packing closely resembles that found in the structure of the *trans*-analogue [2].

The cyclohexane ring has a nearly regular chair conformation; the dihedral angles between the 'seat', defined by C(1), C(2), C(4), C(5) atoms (Table VI, plane 18), and the two three atom planes (Table VI, planes 19 and 20) being 48.4 and 52.5°. The two methine hydrogen atoms of the ring are in a *cis*-conformation and since the complex crystallises in a centric space group both *R,S*- and *S,R*-enantiomers are present in the crystal.

The copper atom has a distorted square-based pyramidal environment with the N_4-tetradentate ligand encompassing the base and a water molecule [Cu–O(W1) 2.382(7) Å] occupying the apical site. The copper atom lies 0.19 Å above the N_4-basal plane (Table VI, plane 1) towards the apical atom. The pyramid is considerably more distorted than that found in the analogous *trans*-structure [2]. The Cu–O(W1) bond direction lies 13.6° from the normal to the N_4-plane towards the open side of the ligand. The increased 'leaning' of this bond eleviates steric interaction between the coordinated water molecule and the cyclohexane ring, in particular the axial hydrogen of carbon atom C(3). Molecular models show that on planar coordination of the ligand a steric interaction occurs between the carboxyl oxygen atom O(1) and the equatorial hydrogen of carbon atom C(6). The out-of-plane distortion which eleviates this situation also defines the apical position of the five-coordinate geometry. That the water molecule is shifted from that apical position once again demonstrates the ability of bivalent copper to distort to eleviate steric interactions such as that described above. The average Cu–N(amide)

TABLE VI. Least-Squares Planes Data.

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

Plane (1): N(11), N(21), N(1), N(2)
N(11) −0.07; N(21) 0.07; N(1) 0.09; N(2) −0.09; Cu −0.19; O(W1) −2.51
Plane (2): O(W1), N(11), N(2)
Cu 0.18
Plane (3): N(21), N(11), N(2)
Cu −0.13
Plane (4): N(1), N(11), N(2)
Cu −0.09
Plane (5): N(11), C(11)–C(15)
N(11) 0.014; C(11) −0.018; C(12) 0.002; C(13) 0.016; C(14) −0.020; C(15) 0.005; Cu 0.09; C(01) −0.01
Plane (6): N(21), C(21)–C(25)
N(21) 0.013; C(21) −0.013; C(22) 0.009; C(23) −0.005; C(24) 0.005; C(25) −0.009; Cu −0.03; C(02) 0.05
Plane (7): N(11), C(11), C(01), N(1)
N(11) 0.013; C(11) −0.023; C(01) 0.023; N(1) −0.013; Cu 0.15; O(1) 0.09; C(12) −0.04; C(15) −0.03
Plane (8): N(21), C(21), C(02), N(2)
N(21) −0.021; C(21) 0.038; C(02) −0.038; N(2) −0.022; Cu −0.35; O(2) −0.16; C(22) 0.25; C(25) 0.07
Plane (9): N(1), C(1), C(2), N(2)
N(1) −0.13; C(1) 0.23; C(2) −0.23; N(2) 0.13; Cu −0.14
Plane (10): C(01), C(11), N(1), O(1)
C(01) −0.001; C(11), N(1), 0(1) < 0.001
Plane (11): C(02), C(21), N(2), O(2)
C(02) 0.003; C(21), N(2), O(2) −0.001
Plane (12): N(1), Cu, C(01)
C(1) 0.44
Plane (13): N(1), Cu, C(1)
C(01) 0.39
Plane (14): N(1), C(01), C(1)
Cu 0.66
Plane (15): N(2), Cu, C(02)
C(2) −0.48
Plane (16): N(2), Cu, C(2)
C(02) −0.41
Plane (17): N(2), C(02), C(2)
Cu −0.68
Plane (18): C(1), C(2), C(4), C(5)
C(1) 0.022; C(2) −0.022; C(4) 0.021; C(5) −0.021; C(3) −0.63; C(6) 0.68
Plane (19): C(6), C(5), C(1)
Plane (20): C(3), C(4), C(2)

Dihedral angles (°) between relevant planes

1–5	13.8	2–3	77.3	12–13	19.3
1–6	9.6	2–4	68.0	12–14	21.1
1–7	14.2	3–4	9.3	13–14	21.7
1–8	8.2			15–16	21.0
5–6	21.0	19–20	4.4	15–17	23.7
5–7	1.6	18–19	48.4	16–17	22.7
6–8	8.3	18–20	52.5		

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):	0.5633	0.0974	−0.8205	2.5640
Plane (2):	0.9387	0.1432	0.3136	3.8060
Plane (3):	0.5083	0.0836	−0.8571	2.2645
Plane (4):	0.6388	0.1032	−0.7624	2.7835

(continued overleaf)

TABLE VI. *(continued)*

	l	*m*	*n*	*p*
Plane (5):	0.7425	0.0480	−0.6681	2.9955
Plane (6):	0.4587	−0.0132	−0.8885	1.8915
Plane (7):	0.7429	0.0194	−0.6691	2.9234
Plane (8):	0.5791	−0.0443	−0.8141	2.7005
Plane (9):	0.6822	0.0116	−0.7311	2.9497
Plane (10):	0.7779	0.0199	−0.6281	2.9527
Plane (11):	0.5789	−0.1367	−0.8038	2.8380
Plane (12):	0.6905	−0.0585	−0.7210	2.8003
Plane (13):	0.6406	0.2720	−0.7181	2.8046
Plane (14):	0.8781	0.1444	−0.4562	3.0585
Plane (15):	0.6960	0.1510	−0.7020	2.9573
Plane (16):	0.3950	0.1480	−0.9067	1.7042
Plane (17):	0.5347	−0.2086	−0.8189	2.7402
Plane (18):	0.0377	−0.7123	−0.7008	2.0448
Plane (19):	0.2704	−0.9556	0.1174	1.3659
Plane (20):	0.2847	−0.9577	0.0419	2.6554

distance of 1.933(8) Å which is as expected shorter than the Cu–N(*pyridine*) distance of 2.027(7) Å, together with other bond lengths and angles within the molecule, are in good agreement with those observed in structures of copper complexes of like ligands [2, 5, 6].

The two pyridine rings are each planar (Table VI, planes 5 and 6) and have a dihedral angle of 21.0° between them, which is the result of their opposite rotations of 1.2 and 21.9°, respectively, relative to the N_4-plane. This arrangement, which is similar to that found for the second molecule in the [Cu(bpen)-H_2O]H_2O structure [6], gives rise to a greater separation (2.16 Å) between the two hydrogen atoms in the 6-positions of the rings than observed in the analogous *trans*-structure [2]. The pyridyl ring (1) is almost coplanar with its amide chelate ring whereas the dihedral angle between the other pyridyl ring and its amide chelate ring is 8.3°.

The two carbonyl carbon atoms exhibit the expected trigonally-planar geometry but the two amide nitrogen atoms are pyramidally distorted. These nitrogen atoms, on average, are distorted about 35% towards a pyramidal structure which is slightly less than twice the distortion observed in the analogous *trans*-structure [2]. In comparison with this latter structure the greater amide nitrogen atom distortion is accompanied by considerably less skewing in the cyclohexane ring.

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