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Studies on the Metal–Amide Bond.
X.* An Evaluation of Molecular Distortions Enforced by Steric Hindrance in the Crystal Structure of [N,N'-Bis(6'-methylpyridine-2'-carboxamido)-1,2-benzene]-copper(II)

ROSS L. CHAPMAN, FREDERICK S. STEPHENS and ROBERT S. VAGG

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

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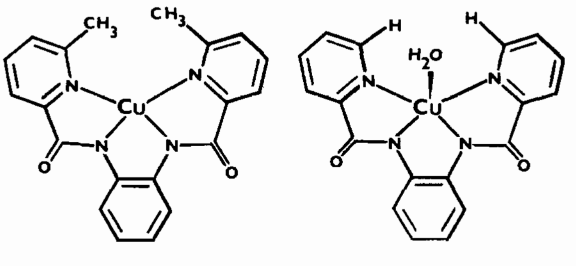
The structure of [N,N'-bis(6'-methylpyridine-2'-carboxamido)1,2-benzene]copper(II) has been determined by photographic methods and refined to R 0.106 for 2090 unique reflexions by least-squares procedures. The monoclinic cell, with space group $P2_1/c$, *has* $a = 10.44(3)$, $b = 14.57(4)$, $c = 11.76(2)$ Å, $\beta = 104.1(2)°$, $Z = 4$. *The ligand acts as a tetradentate through the four N atoms forming a highly distorted square-plane about the Cu atom [average Cu–N(amide) 1.934(7) Å, average Cu–N(pyridine) 2.079(7) Å, N(amide)–Cu–N(amide) 81.3(2)°, N(pyridine)–Cu–N(pyridine) 117.3(2)°]. Amide oxygen atoms of neighbouring molecules coordinate also to form chains parallel to* a *and completing a tetragonally distorted six-coordination [Cu–O(amide) 2.693(6) and 2.798(6) Å]. There is a significant tetrahedral distortion in the* N_4 *geometry of the Cu atom caused by a severe steric interaction between the methyl groups in the 6'-positions of the pyridine rings [*$CH_3 \ldots CH_3$ *separation 3.35(2) Å]. A full analysis of out-of-plane distortions and torsion angles shows that steric strain is relatively uniform throughout the molecule, and that no one atom or bond may be viewed as the major distortion site. A small folding effect in the pyridine rings is observed. The molecular structure parameters are compared with those of the unsubstituted analogue previously reported.*

Introduction

The bis-picolinamide ligands described thus far in this series of papers have each demonstrated a pronounced tendency for planar N_4-tetradentate coordination to transition metal ions on deprotonation. Structural analyses by n.m.r. and X-ray diffraction techniques have indicated close intramolecular contacts of hydrogen atoms in the pyridyl 6'-positions, enforced by this planar mode of coordination [1, and references therein].

In order to enhance such a steric interaction three ligands have been designed [2] in which bulky substituents in these positions might be expected to enforce highly distorted geometries or unfavourable bonding modes on the metal or constituent amide groups. Such effects should be more pronounced in the deprotonated metal chelates of the inflexible ligand 6-mebpbH_2. The bivalent copper complex [Cu(6-mebpb)], I (a), has been isolated in crystalline form and this paper outlines its X-ray structural analysis. The crystal structure of the unsubstituted analogue [Cu(bpb)H_2O], I (b), has been reported previously [3]. A direct comparison of these two molecular structures allows an assessment of the effects of steric hindrance enforced by methyl-substitution. Such an analysis is the subject of the discourse to follow.



(a) [Cu(6-mebpb)]　　(b) [Cu(bpb)H_2O)]

(I)

Experimental

The complex was prepared as previously outlined [2]. Recrystallisation from dimethylsulphoxide yielded dark green needles with [100] elongation.

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*Part IX is reference [2].

Crystal Data

$C_{20}H_{16}N_4O_2Cu$, M_r = 407.93, monoclinic, a = 10.44(3), b = 14.57(4), c = 11.76(2) Å, β = 104.1(2)°, U = 1735 Å^3, D_m = 1.58 (by flotation), Z = 4, D_c = 1.561 Mg m^{-3}, $F(000)$ = 836, μ(Cu-K$_\alpha$) = 2.01 mm^{-1}. Systematic absences: 0k0 when $k \neq 2n$ and h0l when $l \neq 2n$; space group $P2_1/c$ (No. 14).

Cell parameters were determined from oscillation and Weissenberg photographs using Cu-K$_\alpha$ radiation. Utilising the same radiation 2871 non-zero reflexions were recorded on layers 0–6 *kl, h* 0–2 *l* and *hk* 0–2 using the Weissenberg equi-inclination technique. Intensities were estimated visually and corrected for Lorentz and polarization effects but not for absorption or extinction. Internal correlation yielded a final data set of 2090 unique non-zero reflexions. The structure was solved by the heavy atom method. Refinement of the structure was by full matrix least-squares calculations in which the function minimized was $\Sigma w \Delta^2$. The weight for each reflexion, initially unity, was finally given by $w = (1.0 + 0.15|F_o| + 0.004|F_o|^2)^{-1}$. Reflexions for which $|F_o| > 3|F_c|$ were omitted from the least-squares calculations. Positions of hydrogen atoms on the benzene and pyridyl rings were calculated assuming C–H to be 1.0 Å but at no time were their parameters refined. When the maximum shift in any parameter was of the order of its estimated standard deviation a Fourier difference map was calculated. This map showed no unusual features, however, it gave no clear indication of the positions of the methyl hydrogen atoms, therefore these atoms were not included in the structural model. Refinement was continued with anisotropic thermal parameters for all non-hydrogen atoms and was terminated when the maximum shift in any parameter was $<0.1\sigma$. 2073 reflexions were included in the final cycle of refinement. The final value for R based on 2090 reflexions was 0.106, and for R′-$\{=(\Sigma w \Delta^2/\Sigma w|F_o|^2)^{1/2}\}$ was 0.136.

Scattering factors were taken from International Tables for X-ray Crystallography [4]. All calculations were carried out on a UNIVAC 1106 computer with programmes written by F.S.S.. Final atomic parameters are given in Tables I–III. A list of observed and calculated structure factors has been deposited with the Editor.

TABLE I. Final Atomic Coordinates (fractional, × 10^4) for Non-hydrogen Atoms with Estimated Standard Deviations in Parentheses.

	x	*y*	*z*
Cu	2614(1)	344(1)	489(1)
O(1)	5036(7)	508(4)	−1665(5)
O(2)	−440(6)	−1407(4)	44(5)
N(1)	3171(8)	190(5)	−946(6)
N(2)	1481(7)	−679(5)	−164(6)
N(11)	3728(7)	1531(5)	586(6)
N(21)	1988(7)	−31(5)	1978(6)
C(1)	2556(8)	−494(6)	−1709(7)
C(2)	1576(7)	−976(5)	−1282(6)
C(3)	803(10)	−1651(6)	−1976(8)
C(4)	1044(10)	−1873(7)	−3060(8)
C(5)	2017(10)	−1418(7)	−3448(7)
C(6)	2770(9)	−733(6)	−2781(7)
C(11)	4617(8)	1422(5)	−104(6)
C(12)	5660(9)	1993(6)	−60(7)
C(13)	5836(10)	2725(6)	723(9)
C(14)	4915(10)	2887(6)	1369(8)
C(15)	3857(9)	2285(6)	1253(7)
C(21)	896(9)	−555(5)	1645(7)
C(22)	141(10)	−814(6)	2407(8)
C(23)	535(12)	−533(8)	3561(9)
C(24)	1690(12)	−44(8)	3923(7)
C(25)	2413(10)	201(6)	3102(7)
C(01)	4296(8)	640(5)	−995(6)
C(02)	564(9)	−945(6)	406(7)
C(M15)	2741(12)	2511(8)	1832(10)
C(M25)	3756(10)	678(9)	3225(8)

TABLE II. Hydrogen Atomic Parameters (Coordinates: fractional, × 10^3).[a]

	x	*y*	*z*
H(3)	349	−43	−308
H(4)	218	−161	−422
H(5)	50	−235	−356
H(6)	10	−199	−169
H(12)	631	186	58
H(13)	664	315	80
H(14)	501	342	192
H(22)	−67	−120	213
H(23)	−4	−67	414
H(24)	209	12	477

[a] For all H atoms B = 6.0 Å^2.

Discussion

Bond lengths and angles in the molecule are listed in Table IV. Figure 1 shows a perspective drawing [5] of the molecule together with the atomic labelling scheme. The molecular packing arrangement in the cell is shown in Fig. 2.

The ligand acts as a tetradentate through the four nitrogen atoms forming a highly distorted square-plane about the copper atom (Table V, plane 1). Amide-oxygen atoms of neighbouring molecules also coordinate to form chains parallel to the a-axis and completing a tetragonally distorted six-coordination. The two long Cu–O bond lengths [2.693(6) and 2.798(6) Å] are typical of those found in Cu(II) complexes with tetragonally elongated octahedral arrangements [6].

TABLE III. Final 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	58.2(16)	27.7(7)	31.7(9)	−15.3(8)	16.0(9)	−9.8(5)
O(1)	46(7)	26(3)	42(5)	0(4)	20(5)	−5(3)
O(2)	40(7)	25(3)	29(4)	−15(4)	−1(4)	−2(3)
N(1)	53(9)	21(4)	19(4)	−2(5)	12(5)	−8(3)
N(2)	29(7)	13(3)	25(5)	−8(4)	10(5)	7(3)
N(11)	36(8)	19(3)	22(4)	−5(4)	−3(5)	1(3)
N(12)	37(8)	13(3)	25(5)	0(4)	4(5)	1(3)
C(1)	20(8)	18(4)	26(5)	7(5)	15(6)	1(4)
C(2)	2(7)	14(3)	22(5)	3(4)	2(5)	8(3)
C(3)	57(11)	17(4)	43(7)	−11(5)	17(7)	−9(4)
C(4)	48(10)	23(4)	41(7)	−13(6)	3(7)	−16(4)
C(5)	65(11)	32(5)	28(6)	−1(6)	14(7)	−12(4)
C(6)	47(10)	27(4)	20(5)	−5(6)	7(6)	−1(4)
C(11)	26(8)	14(4)	23(5)	6(5)	9(6)	5(4)
C(12)	28(9)	17(4)	38(6)	0(5)	10(6)	11(4)
C(13)	41(10)	20(4)	63(8)	−21(6)	8(8)	3(5)
C(14)	39(10)	18(4)	49(7)	−1(5)	2(7)	−7(4)
C(15)	38(10)	20(4)	33(6)	−5(6)	2(6)	−7(4)
C(21)	41(10)	15(4)	22(5)	14(5)	8(6)	5(4)
C(22)	45(10)	24(4)	37(6)	4(6)	14(7)	14(4)
C(23)	83(13)	38(5)	45(7)	19(7)	41(8)	10(5)
C(24)	89(13)	42(5)	19(6)	7(8)	16(7)	−3(5)
C(25)	55(11)	25(4)	26(6)	4(6)	8(7)	−5(4)
C(01)	18(8)	11(3)	21(5)	8(5)	−7(5)	3(3)
C(02)	36(9)	16(4)	21(5)	6(5)	−1(6)	6(4)
C(M15)	65(12)	45(6)	74(9)	0(8)	34(9)	−25(6)
C(M25)	40(10)	64(7)	34(7)	−22(8)	−1(7)	−19(6)

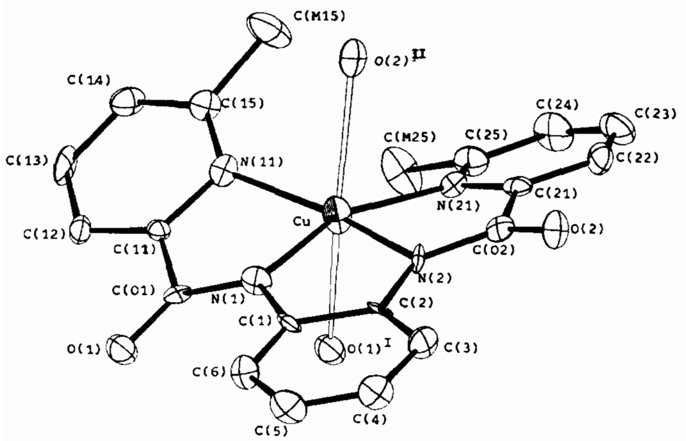

Fig. 1. Perspective drawing of the molecule [5] showing atomic labelling. Thermal parameters are scaled to include 50% probability. Roman numeral superscripts are explained in Table I.

The 1,2-diaminobenzene unit may be considered as the basic plane of the molecule (Table V, plane 6), from which the copper atom is slightly displaced. Deviations away from this central plane increase to the extremities of the ligand, where the pyridyl nitrogen atoms show deviations of the order of 0.5 Å. The dimensions of the amide groups are comparable with those of $[Cu(bpb)H_2O]$ [3] and $[Cu(bpen)H_2O]H_2O$ [7], with the two Cu–N(amide) bond lengths averaging 1.934(7) Å. The Cu–N(pyridine) bond lengths [ave. 2.079(7) Å] are, however, significantly ($\Delta l/\sigma(\Delta l)$ = 7.7 [8]) longer than the 2.023(2) Å observed in the structure of the unhindered complex [3]. The copper atom is displaced only slightly out of the mean plane of the four nitrogen atoms (Table V, plane 1) but there is a significant tetrahedral twist at the metal atom (Table V, planes 2 and 3 intersect at 13.8°). Further distortion away from a square geometry is shown by the N–Cu–N angles. In particular, the large angle between the pyridine nitrogen atoms [117.3(2)°] exemplifies the unusual metal stereochemistry. The two five-membered amide chelate rings. (Table V, planes 7 and 8) are non-planar, which is caused by the Cu atom being displaced from the plane of the other four atoms in each ring.

Distortion within the ligand molecule caused solely by its tetradentate behaviour is demonstrated by the large external angles about the amide carbon atoms, C(01) and C(02), which average 127.6°. Although the familiar *trans* geometry for the amide groups is adopted here, significant distortions away

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

C(1)–C(2)	1.429(11)	C(4)–C(5)	1.381(14)
C(1)–C(6)	1.378(11)	C(2)–C(3)	1.402(12)
C(5)–C(6)	1.390(13)	C(3)–C(4)	1.396(12)
Cu–O(1)^{I}	2.693(6)	Cu–O(2)^{II}	2.798(6)
	n = 1	n = 2	
Cu–N(n)	1.927(7)	1.941(7)	
Cu–N(n1)	2.072(7)	2.085(7)	
N(n)–C(On)	1.360(12)	1.352(11)	
N(n)–C(n)	1.389(11)	1.410(9)	
N(n1)–C(n1)	1.383(11)	1.349(12)	
N(n1)–C(n5)	1.337(11)	1.332(10)	
O(n)–C(On)	1.245(10)	1.231(11)	
C(n1)–C(On)	1.529(10)	1.524(10)	
C(n1)–C(n2)	1.361(12)	1.382(12)	
C(n2)–C(n3)	1.392(13)	1.381(14)	
C(n3)–C(n4)	1.384(15)	1.377(17)	
C(n4)–C(n5)	1.391(13)	1.408(13)	
C(n5)–C(Mn5)	1.522(15)	1.536(14)	
O(1)^{I}–Cu–O(2)^{II}	163.5(2)		
Cu^{I}–O(1)–C(O1)	111.2(2)	Cu^{II}–O(2)–C(O2)	111.4(3)
N(1)–Cu–N(2)	81.3(2)	N(11)–Cu–N(21)	117.3(2)
C(2)–C(1)–C(6)	119.2(5)	C(1)–C(2)–C(3)	120.0(4)
C(1)–C(6)–C(5)	120.1(3)	C(2)–C(3)–C(4)	119.2(9)
N(1)–C(1)–C(2)	112.6(3)	N(2)–C(2)–C(1)	113.3(5)
N(1)–C(1)–C(6)	128.3(5)	N(2)–C(2)–C(3)	126.7(4)
	n = 1	n =2	
O(1)^{I}–Cu–N(n)	88.0(2)	103.4(2)	
O(1)^{I}–Cu–N(n1)	86.0(2)	83.4(2)	
O(2)^{II}–Cu–N(n)	106.3(2)	87.2(2)	
O(2)^{II}–Cu–N(n1)	87.9(2)	85.8(2)	
N(1)–Cu–N(n1)	82.0(2)	158.1(2)	
N(2)–Cu–N(n1)	160.5(2)	81.1(2)	
Cu–N(n1)–C(n1)	108.7(5)	108.7(5)	
Cu–N(n1)–C(n5)	133.9(6)	132.1(6)	
C(n1)–N(n1)–C(n5)	116.9(8)	119.0(7)	
Cu–N(n)–C(On)	115.4(2)	117.5(2)	
Cu–N(n)–C(n)	117.3(3)	115.5(3)	
C(On)–N(n)–C(n)	126.0(4)	126.3(4)	
O(n)–C(On)–N(n)	128.9(5)	129.2(4)	
N(n)–C(On)–C(n1)	112.2(7)	110.1(5)	
O(n)–C(On)–C(n1)	118.4(4)	120.7(2)	
C(On)–C(n1)–N(n1)	114.9(5)	117.9(5)	
C(On)–C(n1)–C(n2)	121.4(4)	119.0(5)	
N(n1)–C(n1)–C(n2)	123.6(5)	122.9(4)	
C(n1)–C(n2)–C(n3)	118.0(4)	118.4(2)	
C(n2)–C(n3)–C(n4)	119.8(4)	119.1(4)	
C(n3)–C(n4)–C(n5)	118.7(8)	119.7(8)	
C(n4)–C(n5)–N(n1)	122.7(4)	120.8(4)	
N(n1)–C(n5)–C(Mn5)	117.5(5)	119.6(5)	
C(Mn5)–C(n5)–C(n4)	119.7(3)	119.5(3)	

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[a] Roman numerals as superscripts refer to atoms at:
I $(1 - x, \bar{y}, \bar{z})$
II $(\bar{x}, \bar{y}, \bar{z})$

TABLE V. 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.

Plane No.	Atoms Defining Plane	l	m	n	p
1	N(11), N(21), N(1), N(2)	0.8010	−0.5668	0.1926	1.8503
2	Cu, N(11), N(21)	0.8363	−0.5339	0.1247	1.9353
3	Cu, N(1), N(2)	0.7078	−0.6406	0.2977	1.5261
4	N(11), C(11)–C(15)	0.5557	−0.5547	0.6193	0.6614
5	N(21), C(21)–C(25)	0.5341	−0.8418	0.0780	1.2825
6	N(1), N(2), C(1)–C(6)	0.6813	−0.6769	0.2786	1.5053
7	N(1), C(O1), C(11), N(11)	0.5343	−0.6312	0.5622	0.4644
8	N(2), C(O2), C(21), N(21)	0.5410	−0.8154	0.2058	1.5009
9	O(1), C(11), N(1)	0.5416	−0.6335	0.5527	0.5048
10	O(2), C(21), N(2)	0.5264	−0.8258	0.2027	1.4910

b) Deviations (Å) of relevant atoms from least-squares planes defined above.

Plane	
1	N(11) −0.14; N(21) 0.14; N(1) −0.20; N(2) 0.20; Cu −0.03.
4	N(11) 0.040; C(11) −0.014; C(12) −0.020; C(13) 0.030; C(14) −0.004; C(15) −0.31; Cu 0.48; C(01) −0.16; C(M15) −0.24.
5	N(21) −0.027; C(21) 0.016; C(22) 0.010; C(23) −0.24; C(24), C(25) 0.013; Cu −0.30; C(O2) 0.21; C(M25) 0.17.
6	N(1) −0.038; N(2) 0.028; C(1), C(4) 0.013; C(2) 0.005; C(3) 0.022; C(5) −0.014; C(6) −0.028; Cu −0.07; C(O1) 0.20; C(O2) −0.09; N(11) −0.51; N(21) 0.40.
7	N(1), C(O1), C(11), N(11) $<\lvert 0.001\rvert$; Cu 0.58; O(1) −0.03.
8	N(2), C(O2), C(21), N(21) $<\lvert 0.001\rvert$; Cu −0.50; O(2) −0.04.
9	C(O1) 0.011
10	C(O2) 0.014

c) Dihedral angles (°) between relevant planes

1–4	28.5	6–4	22.1	4–5	35.7
1–5	23.1	6–5	17.2	7–8	23.2
1–6	10.6	6–7	18.6	4–7	5.6
1–7	26.6	6–8	12.1	5–8	7.5
1–8	20.7				
2–3	13.8				

from planarity are obvious. The amide carbon atoms show small deviations from trigonal planarity (Table V, planes 9 and 10, and Table VI (a)). Dihedral angles between the mean planes of the pyridyl rings (Table V, planes 4 and 5) and the central 1,2-diaminobenzene plane (plane 6) are 22.1 and 17.2° for rings 1 and 2 respectively. The methyl carbon atoms show relatively large deviations from the least-squares planes of the associated pyridine rings indicating significant strain at the attached α-carbon atoms. The methyl carbon atoms are 3.35(2) Å apart, some 0.65 Å less than the sum of the van der Waals radii for two methyl groups [9].

This very close contact reflects a severe form of 'B'-strain [10] enforced in the ligand molecule, to which out-of-plane distortions may be attributed. A closer evaluation of its effects shows that small but significant distortions *within* the pyridine rings exist also. These take the form of a folding along the N(n1)....C(n3) direction, thus producing a 'boat'

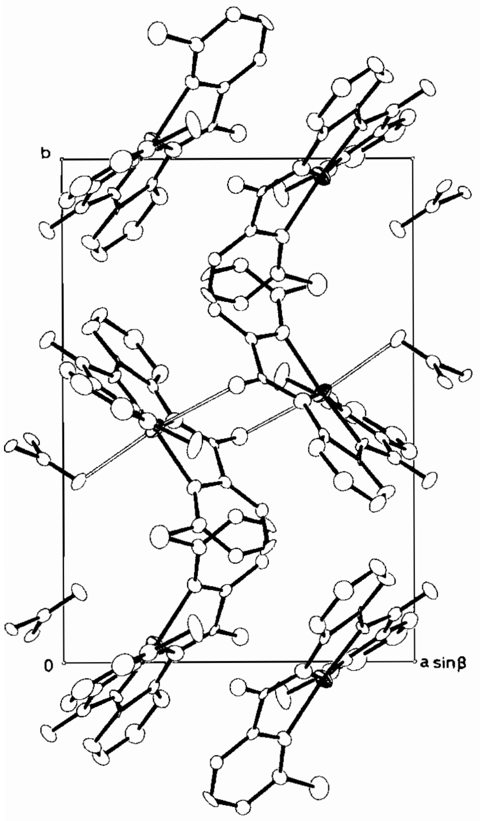


Fig. 2. The packing of the molecules in the unit cell, showing the formation of chains parallel to *a*.

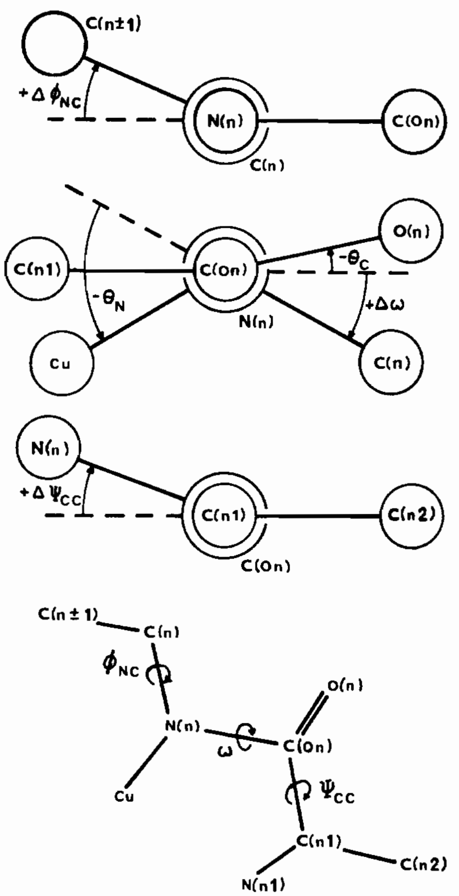


Fig. 3. Torsion angles and specific distortions about the 'peptide unit'.

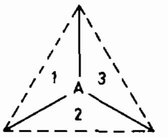
distortion for each ring. A full analysis of distortions from planarity, together with the torsion angles in the 'peptide units', are given in Table VI. The notations used are described in Fig. 3. In this Table a direct comparison of relevant parameters is made with those in the unhindered analogue [Cu(bpb)H_2O] [3]. Differences, therefore, may be attributed to the different degree of substitution on the pyridine rings. The overall effect may be readily appreciated by the molecular projections shown in Fig. 4.

It may be seen from Table VI that [Cu(bpb)H_2O] shows, as expected, the smaller degree of distortion. The relatively large $\Delta\phi_{NC}$ value (+12.5°) for only one of the N(n)–C(n) bonds (n = 2) of this molecule shows that relief of steric strain caused by the H(15)....H(25) interaction is achieved by only one picolinamide unit twisting away from the plane of the rest of the molecule. This is accompanied by a small pyramidal distortion at amide-N(2). These observations are consistent with the dihedral angle of 12.8° previously described [3].

The distorting effects of methyl-substitution are obvious in almost all of the structural parameters presented. The complex [Cu(6-mebpb)] shows pyramidal distortions about the amide-nitrogen atoms, the pyridine-nitrogen atoms and the adjacent C(n5) atoms also (Table VI). Both pyridine rings demonstrate relatively large 'folding' angles which appear to have a twofold effect; as well as relieving the hindering effects of the methyl groups this distortion alleviates, to some degree, the pyramidal distortions about the pyridine-nitrogen atoms. In this molecule the θ_C values are quite small. This finding is in agreement with the CNDO/2 calculations of Ramachandran *et al.* [11] for N-methyl-acetamide, who concluded that pyramidal distortion is more readily achieved about the N-atom than about the carboxyl-C atom of an amide group. The observation that both $\Delta\omega$ and $\Delta\phi_{NC}$ are reasonably large and of the same sign for the [Cu(6-mebpb)] molecule indicates that the 'twisting away' effect of the two methylpicolinamide units is uniform for both halves of the molecule. The reversal of this trend for $\Delta\psi_{CC}$ probably reflects the increase in length and distortion of the Cu–N(pyridine) bonds as the pyridyl rings twist further out of the –(CO)–N–M–N– (CO)– plane. The significantly greater average Cu–N-(pyridine) in [Cu(6-mebpb)] compared with that in [Cu(bpb)(H_2O)] again demonstrates this steric effect.

TABLE VI. Molecular Distortion Parameters.

a) Pyramidal distortions about selected atoms, expressed as the average interplanar angle (°) between planes 1, 2 and 3.



A	Cu(bpb)H_2O		Cu(6-mebpb)	
	n = 1	n = 2	n = 1	n = 2
C(On)	0.5	1.9	1.6	2.0
N(n)	0.7	7.8	13.2	9.9
N(n1)	5.9	1.1	8.9	4.9
C(n5)	–	–	4.2	4.6

b) Distortions away from planarity within the pyridyl ring

γ = dihedral angle between planes containing C(n1), N(n1), C(n5) and C(n2), C(n3), C(n4)

δ = dihedral angle between planes containing N(n1), C(n1), C(n2), C(n3) and N(n1), C(n3), C(n4), C(n5)

	Cu(bpb)H_2O		Cu(6-mebpb)	
	n = 1	n = 2	n = 1	n = 2
$\|\gamma\|$	0.5	1.8	8.5	6.3
$\|\delta\|$	0.2	0.9	5.1	3.7

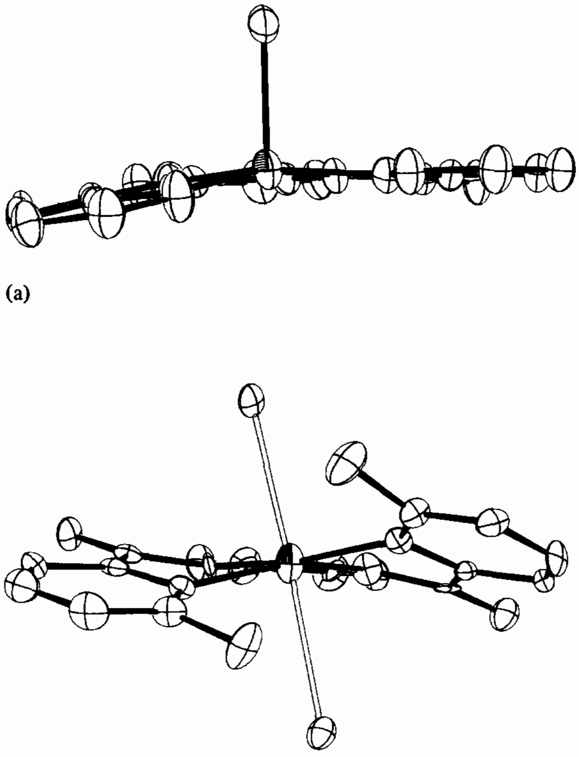
c) Torsion angles and specific distortions about the 'peptide unit'*

Parameters	Cu(bpb)H_2O		Cu(6-mebpb)	
	n = 1	n = 2	n = 1	n = 2
$\Delta\psi_{CC}$	+3.3	−1.0	+4.0	+5.6
$\Delta\omega$	+1.2	−5.8	−6.2	−6.5
θ_N	−0.9	+8.2	−13.5	−10.2
θ_C	+0.3	−1.9	−1.7	−2.3
$\Delta\phi_{NC}$	−4.6	+12.5	−13.4	−6.8

*Definition of 'peptide unit' (with Cu replacing H) and notation for torsion angles from Edsall *et al.* [18] and I.U.P.A.C. - I.U.B. Conventions [19]. θ_N and θ_C from Ramachandran *et al.* [11]. The equations of planes defining distortions are given in Table VII (deposited with the Editor).

Quantum-chemical calculations [11, 12] on model peptide systems have shown that often there may be significant non-planar distortions about the nitrogen atom. These calculations also have indicated that $\Delta\omega$ and θ_N are correlated approximately through the relationship:

$$\theta_N = -2\Delta\omega$$



(a)

(b)

Fig. 4. Perspective drawings of (a) [Cu(bpb)H_2O] and (b) [Cu(6-mebpb)], both viewed between the pyridine rings towards the central Cu atoms. Comparison of the two projections demonstrates distortions from planarity due to methyl-substitution.

An analysis of crystal structures of peptides has shown that this relationship is supported by that data [11]. The angular distortions about the amide groups in [Cu(bpb)H_2O)] fit this relationship reasonably well. That these values for [Cu(6-mebpb)] have similar signs is an indication of its enforced geometry.

The distortions about the amide group in this molecule are considerably greater than those reported by Freeman [13] as being the limits to which peptide groups can be deformed in order to accommodate 'ring strain'. A recent crystal structure analysis of (*L*-methionylglycinato)copper(II) [14], a compound possessing amide groups coordinated to different metal atoms through both the deprotonated amide-N and -O atoms, gave a $\Delta\omega$ value of −4.0°, again somewhat lower than values found for [Cu(6-mebpb)].

The results of this structural analysis highlight the strong tendency for ligands containing two or more deprotonated amide/peptide nitrogen atoms to coordinate in a planar arrangement about a metal atom. This general observation has been demonstrated previously for a considerable range of ligands including peptides [13], biuret and substituted biurets [15], oxamides and substituted oxamides [16]. For the bis-amide ligands studied in this work it appears that this geometry is retained even when large unfavourable steric effects result. The significant enforced strain in the title complex is reduced by a relatively uniform distortion over the entire molecule. In general no one atom or bond can be shown to be the major distortion site. A different effect was observed in the structures of the deprotonated copper(II) and nickel(II) complexes of bpchH$_2$ [17]. In these complexes relief of steric strain is provided mainly by large pyramidal distortions about the amide-N atoms alone.

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