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Studies on the Metal–Amide Bond. II*. The Crystal Structure of the Deprotonated Copper(II) Complex of N,N′-Bis-(2′-pyridinecarboxamide)-1,2-benzene

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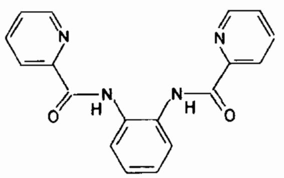
Aqua[N,N′-bis(2′-pyridinecarboxamido)-1,2-benzene]copper(II), $C_{18}H_{14}N_4O_3Cu$, *is triclinic, space group* $P\bar{1}$, *with* a = *7.443(3),* b = *9.560(2),* c = *11.197(4)* Å, α = *92.63(2),* β = *100.02(2),* γ = *84.50(2)°, Z = 2. The structure was refined to* R = *0.038 for 2813 diffractometer data using least-squares methods. The copper atom is five-coordinate, the ligand acting as a planar* N_4 *tetradentate in encompassing the base of a distorted square-based pyramid [Cu–N(*amide*) 1.933(2)* Å, *average Cu–N (*pyridine*) 2.023(2)* Å, *N(*amide*)–Cu–N(*amide*) 82.8°, N(*pyridine*)–Cu–N(*pyridine*) 110.7°] and with the Cu atom raised 0.19* Å *above the* N_4 *plane towards the apical water molecule (Cu–O 2.286(2)* Å*). The water molecule hydrogen bonds carbonyl oxygen atoms of adjacent chelate molecules, which are packed in layers parallel to* $(21\bar{2})$*. An intramolecular steric interaction between the two H atoms in the 6-positions of the pyridine rings (H····H 1.98* Å*) is evident.*

Introduction

Recently we reported the synthesis of a number of potentially tetradentate bis-amide ligands derived from piclonic acid and various diamines [1]. One such ligand, N,N′-bis(2′-pyridinecarboxamide)-1,2-benzene, ($bpbH_2$) (I) has been shown to coordinate to transition metal ions as a planar N_4 tetradentate resulting in a marked increase in the lability of the amide protons [2]. The copper(II) chloride complex of $bpbH_2$ is readily deprotonated in solution under basic conditions or by heating to 160 °C in the solid state with consequent loss of hydrogen chloride [2]. An analysis of the crystal structure of the resultant deprotonated copper(II) chelate, [Cu(bpb)(H_2O)], is described below.



(I)

Experimental

The complex was prepared by the reaction of copper(II) acetate with $bpbH_2$ as described earlier [2]. Recrystallization from pyridine yielded dark green-brown truncated rhomboids.

Crystal Data

$C_{18}H_{14}N_4O_3Cu$, M_r = 397.9, Triclinic, a = 7.443(3) b = 9.560(2), c = 11.197(4) Å, α = 92.63(2), β = 100.02(2), γ = 84.50(2)°, U = 780.6 Å^3, D_m = 1.68 (by flotation), D_c = 1.693 Mg m^{-3}, Z = 2, $F(000)$ = 406, μ(Cu-K$_\alpha$) = 21.9 cm^{-1}. Space group $P1$ (No. 1) or $P\bar{1}$ (No. 2).

Initially, unit cell parameters were determined from single crystal precession photographs using Mo-K$_\alpha$ radiation. Accurate cell parameters were obtained from a least-squares fit to diffractometer data. Intensities were collected on a Siemens AED four-circle diffractometer with monochromatic Cu-K$_\alpha$ radiation. A $\theta/2\theta$ scanning technique with integrated intensities was employed, the beam being attenuated with Ni foils for strong reflexions. Each unique reflexion in the $hk\bar{1}3$–13 range was recorded. 2831 unique reflexions gave counts for which $I > 2\sigma(I)$ and these were used for the structure analysis. Intensities were corrected for Lorentz, polarization and absorption effects [3] but no correction for extinction was applied. Scattering factor curves were taken from *International Tables for X-Ray Crystallography* [4]. All calculations were carried out on a UNIVAC 1106 computer using programmes written by F.S.S..

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*Part I is reference [2].

TABLE I. Final Atomic Coordinates (Fractional, $\times 10^4$ for Non-hydrogen Atoms, $\times 10^3$ for Hydrogen Atoms) with Estimated Standard Deviations in Parentheses.

	x/a	y/b	z/c
Cu	4145.4(5)	4705.4(4)	1909.0(3)
O(W)	1987(3)	3677(3)	2705(2)
O(1)	1027(3)	6813(2)	−871(2)
O(2)	6834(3)	6697(2)	4836(2)
N(1)	2779(3)	6247(2)	998(2)
N(2)	4791(3)	6181(2)	3093(2)
N(11)	3393(3)	3626(2)	335(2)
N(21)	6160(3)	3580(3)	3012(2)
C(1)	2791(4)	7547(3)	1624(2)
C(2)	3907(4)	7517(3)	2798(2)
C(3)	4032(4)	8733(3)	3508(3)
C(4)	3066(5)	9988(3)	3087(3)
C(5)	1984(5)	10018(3)	1942(3)
C(6)	1858(4)	8810(3)	1206(3)
C(11)	2293(4)	4451(3)	−493(2)
C(12)	1507(4)	3908(3)	−1605(3)
C(13)	1851(5)	2501(4)	−1877(3)
C(14)	2958(5)	1669(4)	−1046(3)
C(15)	3694(5)	2261(3)	58(3)
C(21)	6883(4)	4356(3)	3976(2)
C(22)	8271(4)	3805(3)	4851(3)
C(23)	8956(5)	2426(4)	4731(3)
C(24)	8230(5)	1627(4)	3765(3)
C(25)	6810(5)	2240(4)	2926(3)
C(01)	1957(4)	5986(3)	−139(2)
C(02)	6143(4)	5892(3)	4020(2)
H(3)	481	872	434
H(4)	315	1088	360
H(5)	129	1093	164
H(6)	108	885	37
H(12)	70	454	−221
H(13)	129	209	−269
H(14)	322	62	−122
H(15)	448	163	68
H(22)	879	441	557
H(23)	1003	202	534
H(24)	872	61	365
H(25)	622	163	223
H(W1)	127	341	242
H(W2)	205	351	332

Structure Determination

Since the cell contains 2 formula units the space group $P\bar{1}$ was assumed in initial calculations; this was later confirmed by the successful refinement of the structure. A Patterson synthesis gave the positions of the metal atom and its coordination sphere; a Fourier synthesis phased by these atoms then yielded the positions for all non-hydrogen atoms. Refinement was carried out using full-matrix least-squares calculations in which the function minimized was $\Sigma w\Delta^2$. The weights for each reflexion, initially unity, were given by $w = (1.00 \pm 0.10|F_o| + 0.0018|F_o|^2)^{-1}$ in the latter stages of refinement. For this scheme average values of $w\Delta^2$ for ranges of increasing $|F_o|$ were nearly constant. Reflexions for which $|F_c| < 0.33|F_o|$ were omitted from the least-squares analysis.

After the initial isotropic refinement a difference synthesis indicated the positions of the hydrogen atoms on the atomatic rings. These positions were optimized assuming C–H to be 1.00 Å and refinement was continued with H atoms located in these positions with $B = 5.0$ Å^2, their parameters not being refined.

Final refinement included anisotropic thermal parameters for all non-hydrogen atoms. After several cycles a difference map indicated the positions of the two H atoms of the water molecule. These positions each showed peaks of height 0.7 eÅ^{-3} and were the only maxima greater than 0.3 eÅ^{-3} in the map. Subsequently H atoms were held in those positions with $B = 5.0$ Å^2. Refinement was terminated when the maximum shift in any parameter was $<0.13\sigma$. 2813 reflexions were included in the final cycle, R based on these data being 0.038 and R' $[=(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}]$ being 0.054. A final difference map showed no peaks greater than $|0.3|$ eÅ^{-3}. The final atomic parameters are given in Tables I and II. A list of structure factors has been deposited with the Editor.

Discussion

Bond lengths and angles in the molecule, together with estimated standard deviations, are listed in Table III.

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	161.0(9)	88.4(5)	61.4(4)	4.6(4)	−9.4(4)	−0.8(3)
O(W)	191(5)	128(3)	61(2)	−51(3)	−8(2)	14(2)
O(1)	208(5)	88(2)	56(2)	3(3)	−28(2)	10(2)
O(2)	225(5)	92(2)	61(2)	−23(3)	−45(2)	−1(2)
N(1)	127(4)	72(2)	49(2)	−5(3)	−12(2)	1(2)
N(2)	126(4)	72(2)	49(2)	−4(3)	−10(2)	2(2)
N(11)	141(4)	81(3)	51(2)	7(3)	2(2)	−2(2)
N(21)	137(4)	82(3)	58(2)	14(3)	−11(2)	1(2)

(continued on facing page)

TABLE II. *(Continued)*

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	122(5)	68(3)	54(2)	−8(3)	2(3)	5(2)
C(2)	117(5)	69(3)	55(2)	−10(3)	2(2)	2(2)
C(3)	189(6)	83(3)	65(3)	−13(4)	−8(3)	−3(2)
C(4)	236(7)	72(3)	83(2)	−9(4)	−5(4)	−7(2)
C(5)	214(7)	69(3)	91(3)	5(4)	−7(4)	6(2)
C(6)	169(6)	74(3)	70(3)	−7(3)	−10(3)	9(2)
C(11)	124(5)	84(3)	43(2)	−8(3)	7(2)	1(2)
C(12)	175(6)	105(4)	48(2)	−12(4)	−2(3)	−3(2)
C(13)	231(7)	109(4)	57(2)	−12(4)	18(3)	−19(2)
C(14)	263(8)	95(4)	73(3)	15(4)	1(4)	−19(3)
C(15)	212(7)	89(3)	70(3)	20(4)	−12(3)	−10(2)
C(21)	113(5)	85(3)	53(2)	−11(3)	1(3)	10(2)
C(22)	168(6)	103(4)	69(3)	−6(4)	−27(3)	14(2)
C(23)	193(7)	119(4)	82(3)	19(4)	−35(4)	23(3)
C(24)	229(8)	103(4)	94(3)	50(4)	20(4)	7(3)
C(25)	236(8)	95(4)	81(3)	40(4)	−34(4)	−10(2)
C(01)	123(5)	83(3)	48(2)	−7(3)	0(2)	6(2)
C(02)	128(5)	79(3)	51(2)	−12(3)	−3(3)	7(2)

*For all hydrogen atoms $B = 5.0$ Å^2.

TABLE III. Bond Lengths (A) and Angles (°) with Estimated Standard Deviations in Parentheses.

Cu–O(W)	2.286(2)		
C(1)–C(2)	1.428(4)	C(2)–C(3)	1.381(4)
C(3)–C(4)	1.395(4)	C(4)–C(5)	1.390(5)
C(5)–C(6)	1.389(4)	C(6)–C(1)	1.392(4)

	n = 1	*n* = 2
Cu–N(*n*)	1.933(2)	1.933(2)
Cu–N(*n*1)	2.021(2)	2.025(2)
N(*n*)–C(*n*)	1.398(3)	1.404(3)
N(*n*)–C(O*n*)	1.337(3)	1.332(3)
N(*n*1)–C(*n*1)	1.353(3)	1.343(4)
N(*n*1)–C(*n*5)	1.335(4)	1.331(4)
O(*n*)–C(O*n*)	1.239(3)	1.241(3)
C(*n*1)–C(O*n*)	1.511(4)	1.520(4)
C(*n*1)–C(*n*2)	1.381(4)	1.377(4)
C(*n*2)–C(*n*3)	1.375(4)	1.376(5)
C(*n*3)–C(*n*4)	1.361(5)	1.358(5)
C(*n*4)–C(*n*5)	1.381(4)	1.389(4)

N(1)–Cu–N(21)	161.1(1)	N(2)–Cu–N(11)	163.3(1)
N(1)–Cu–N(2)	82.8(1)	N(11)–Cu–N(21)	110.7(1)
N(1)–C(1)–C(2)	114.0(1)	N(2)–C(2)–C(1)	113.4(2)
N(1)–C(1)–C(6)	126.5(2)	N(2)–C(2)–C(3)	127.0(3)
C(2)–C(1)–C(6)	119.5(2)	C(1)–C(2)–C(3)	119.6(2)
C(1)–C(6)–C(5)	119.9(2)	C(2)–C(3)–C(4)	120.4(3)
C(6)–C(5)–C(4)	120.7(1)	C(3)–C(4)–C(5)	119.9(3)

	n = 1	*n* = 2
O(W)–Cu–N(*n*)	104.3(1)	102.3(1)
O(W)–Cu–N(*n*1)	88.6(1)	90.2(1)
N(*n*)–Cu–N(*n*1)	82.2(1)	82.2(1)
Cu–N(*n*1)–C(*n*1)	111.4(1)	111.8(2)
Cu–N(*n*1)–C(*n*5)	130.0(2)	130.2(2)

TABLE III. *(continued)*

Cu–N(*n*)–C(O*n*)	118.4(1)	118.5(1)
Cu–N(*n*)–C(*n*)	114.6(1)	114.9(1)
C(O*n*)–N(*n*)–C(*n*)	127.0(1)	126.2(1)
C(*n*1)–C(O*n*)–N(*n*)	110.0(2)	112.2(2)
O(*n*)–C(O*n*)–N(*n*)	128.7(2)	128.8(2)
C(*n*1)–N(*n*1)–C(*n*5)	118.3(2)	118.0(2)
O(*n*)–C(O*n*)–C(*n*1)	120.3(2)	120.0(2)
C(O*n*)–C(*n*1)–N(*n*1)	116.9(2)	116.4(2)
C(O*n*)–C(*n*1)–C(*n*2)	121.8(1)	121.7(2)
N(*n*1)–C(*n*1)–C(*n*2)	121.4(1)	121.9(1)
C(*n*1)–C(*n*2)–C(*n*3)	119.3(1)	119.2(1)
C(*n*2)–C(*n*3)–C(*n*4)	119.5(2)	119.5(2)
C(*n*3)–C(*n*4)–C(*n*5)	118.9(3)	118.4(3)
C(*n*4)–C(*n*5)–N(*n*1)	112.6(2)	122.9(1)

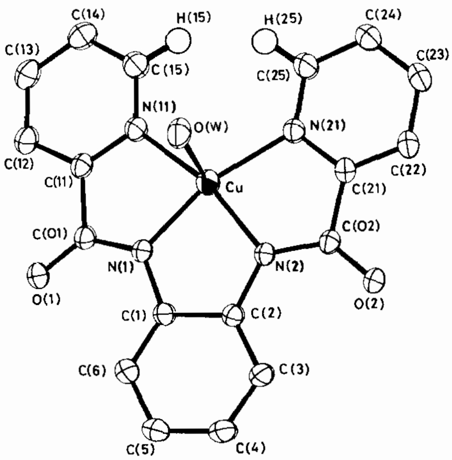

Fig. 1. Perspective drawing [5] of the molecule showing the labelling of the atoms. Thermal ellipsoids for non-hydrogen atoms are scaled to include 35% probability.

TABLE IV. Least-Squares Planes Data.*

(a) *Deviation (Å) of relevant atoms from least-squares planes.*

Plane (1): N(1), N(2), N(11), N(21)
N(1) 0.034; N(2) -0.034; N(11) -0.026; N(21) 0.026; Cu -0.187.

Plane (2): N(1), N(2), C(1)–C(6)
N(1) -0.007; N(2) 0.006; C(1) -0.002; C(2), C(4) -0.003; C(3) 0.013; C(5) 0.005; C(6) 0.002; Cu -0.124; C(01) 0.076; C(02) 0.240; N(11) 0.034; N(21) 0.192

Plane (3): N(11), C(11)–C(15)
N(11), C(14) 0.004; C(11), C(13) < 0.001; C(12) -0.002; C(15) -0.007; Cu 0.145; O(1) 0.042; C(01) -0.011.

Plane (4): N(21), C(21)–C(25)
N(21) 0.008; C(21) 0.002; C(22) -0.008; C(23) 0.006; C(24) 0.004; C(25) -0.011; Cu 0.013; O(2) 0.160; C(02) 0.066.

Plane (5): N(1), N(11), C(11), C(01)
N(1) -0.008; N(11) 0.008; C(11) -0.013; C(01) 0.013; Cu -0.068; O(1) 0.053; C(1) 0.027.

Plane (6): N(2), N(21), C(21), C(02)
N(2) -0.010; N(21) 0.010; C(21) -0.016; C(02) 0.016; Cu -0.005; O(2) 0.091; C(2) 0.123.

Plane (7): N(1), O(1), C(11)
C(01) -0.002; Cu < 0.001; N(11), 0.063; C(1) 0.020.

Plane (8): N(2), O(2), C(21)
C(02) -0.012; Cu 0.102; N(21) 0.094; C(2) 0.108

Plane (9): N(11), O(W), N(2)
Cu -0.199

Plane (10); N(1), O(W), N(21)
Cu -0.188

Plane (11): N(1), N(2), N(11)
Cu -0.148

Plane (12): N(2), N(11), N(21)
Cu -0.163

Plane (13): N(1), N(11), N(21)
Cu -0.211

Plane (14): N(1), N(2), N(21)
Cu -0.227

(b) *Dihedral angles (°) between relevant planes:*

1–2	3.1	9–11	105.1
1–3	4.6	9–12	101.4
1–4	6.8	11–12	176.3
2–3	1.4	10–13	104.2
2–4	12.8	10–14	100.5
2–5	2.7	13–14	176.3
2–6	9.0		

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*Details of the equations for the planes have been deposited with the Editor.

Figure 1 shows a perspective drawing of the molecule together with the atomic labelling, and Fig. 2 the packing arrangement of the molecules in the cell [5].

The water molecule, represented by O(W), is coordinated to the copper atom (Cu–O(W) 2.286(2) Å) and also forms hydrogen bonds with carbonyl oxygen atoms of adjacent chelate molecules [O(W)–H(W1)····O(1) at $(\bar{x}, 1 - y, \bar{z})$ = 2.825(3) Å; O(W)–H(W2)····O(2) at $(1 - x, 1 - y, 1 - z)$ = 2.769(3) Å]. As a result the crystal structure consists of a series of layers parallel to $(21\bar{2})$ linked by the bonding capacities of the water molecules (Fig. 2).

The formation of a crystalline product is thus largely dictated by the hydrogen and coordinate bonding demands of its oxygen atoms; hence the monohydrate form was successfully recrystallised from pyridine [2] without replacement of the water molecule by the heterocyclic base.

The copper atom is five-coordinate, with the ligand acting as a tetradentate in encompassing the basal plane of a distorted square pyramidal geometry

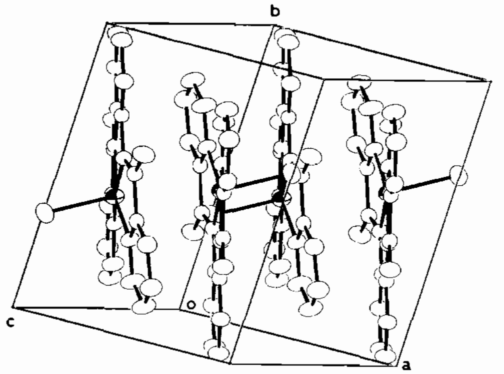

Fig. 2. Molecular packing in the cell. The four molecules have been chosen to best demonstrate the planar nature of the packing.

(Fig. 1). The metal atom is raised slightly (0.19 Å) out of the plane of the four nitrogen atoms (Table IVa, plane 1) towards O(W) coordinated in the apical position. The nearest intermolecular contact to the copper atom in what would constitute a distorted octahedral geometry is that of 3.49 Å to C(11) at $(1 - x, 1 - y, \bar{z})$, a distance greater than the sum of the van der Waals radii [6] for the participating atoms.

The 1,2-diaminobenzene unit and the two pyridyl rings are all planar (Table IVa, planes 2, 3 and 4 respectively), with the metal atom being only slightly displaced from each plane. The same is true of the two picolinamide five-membered coordination rings (planes 5 and 6). It is of some interest that the C(1)–C(2) bond (1.428(4) Å) is significantly longer than the other five C–C bonds (average 1.389(6) Å) in the benzene ring (Table III).

The greatest deviation from planarity in the ligand is demonstrated by the rotation of 12.8° of pyridyl ring 2 away from the central 1,2-diaminobenzene plane (Table IVb). This effect would appear to be due to the close intramolecular contact that occurs between the two H atoms in the 6-positions of the pyridyl rings enforced by the planar tetradentate function of the ligand. The H(15)····H(25) contact distance in the structure is 1.98 Å, much less than the sum of the van der Waals radii [6], signifying an effect that would become more extreme if the ligand were completely planar.

The consequential effect on the geometry of the copper atom is a slight distortion away from a square pyramid to a trigonal bipyramid. This change is aided by a marked 'leaning' of the Cu–O(W) bond towards the open side of the ligand. A measure of the degree of this distortion is gained from a comparison of the dihedral angles between planes 9 to 14 in Table IVb. These angles compare with 90 and 180° expected for an undistorted square pyramid, and 120° for a trigonal bipyramid.

The two Cu–N (*amide*) bonds (1.933(2) Å) are significantly shorter than those to the pyridyl N atoms (*av.* 2.023(2) Å), the former being comparable with Cu–N (*peptide*) bonds [7]. The two amide groups have the commonly observed *trans*-planar geometry [7–9] which is necessarily enforced by the ligand's multidentate function. The bond dimensions of these groups (Table III) are very similar to comparable structures and again reflect their tautomeric nature [8, 9].

Acknowledgements

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