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Structural Researches on Copper(II) Complexes with Vitamin B_6 Derivatives: X-Ray Structure of *trans*-Bis(N-n-butyl-pyridoxylideneiminato)Copper(II)

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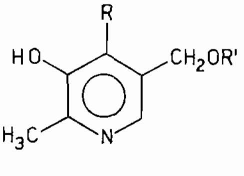
The structure of the title compound has been determined by X-ray methods. Crystals are monoclinic, space group C2/c *with Z = 4 in a unit cell of dimensions* a *= 21.992(11),* b *= 7.788(3),* c *= 17.604(12) Å, β = 128.05(3)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to* R *= 0.0377 for 1443 independent observed reflections. The copper atom lies on a two-fold axis and is chelated to two pyridoxylidene ligands through the imino N and the phenolate O in a* trans-*configuration with a θ value of 15.9(2)°. The complexes adopt a butterfly arrangement and are held together by a weak hydrogen bond so forming zig-zag strip-like chains.*

Introduction

Vitamin B_6, whose basic structure can be schematically represented by:



is found in natural foods in various forms which differ from the R and R′ substitutes. Pyridoxal (R = –CHO, R′ =H) is one of the most biologically active B_6 vitamers and plays an important part in some enzymatic reactions in the presence of metal ions. Since there is every reason to believe that the chelation and catalysis phenomena are related, we have determined the structure of the copper(II) complex with N-pyridoxylidene-n-butylamine. Few Cu(II) complexes with B_6 vitamers were structurally studied but no pyridoxylidene derivative acting exclusively as bidentated ligand [1–5].

Experimental

Synthesis of the Complex

The complex was prepared following the reference [6] and recrystallized from methanol. Elemental C, H, N analyses (made on a Perkin-Elmer Mod. 240 automatic analyser) and Cu electro-gravimetric determinations were carried out in order to attest stoichiometry.

Crystal Data

$C_{24}H_{34}CuO_4N_4$, M = 506.103, monoclinic, a = 21.992(11), b = 7.788(3), c = 17.604(12) Å, β = 128.05(3)°, V = 2374(2) Å^3, Z = 4, D_c = 1.42, D_m = 1.40 Mg m^{-3} $F(000)$ = 1068, MoK_α radiation, λ = 0.71069 Å, μ(MoK_α) = 9.567 cm^{-1}, space group $C2/c$ from systematic absences.

A green plate-like crystal of the compound with dimensions of *ca.* 0.06 × 0.29 × 0.53 mm^3 was used for the data collection. Preliminary cell parameters determined by rotation and Weissenberg photographs were successively refined by a least-squares procedure applied to the θ values of 18 reflections accurately measured on a Siemens AED single crystal diffractometer.

Intensity Data

Intensity data were collected at room temperature on the same diffractometer using zirconium-filtered MoK_α radiation and the ω–2θ scan technique. The intensity of a standard reflection was measured after 20 reflections as a check on crystal and instrument stability. A total of 1849 independent reflections was measured up to θ = 24°, and of these 1443 having $I \geqslant 2\sigma(I)$ were considered observed and therefore used in the analysis. The structure amplitudes were obtained after the usual correction for Lorentz and polarization factors and the absolute

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TABLE I. Fractional Atomic Coordinates (×10^4) for Non-Hydrogen Atoms with e.s.d.s in Parentheses.

	x/a	y/b	z/c
Cu	0	2075(1)	2500
O(1)	742(2)	1803(5)	3857(3)
O(2)	2517(2)	−1570(6)	3247(3)
N(1)	833(2)	2286(6)	2376(3)
N(2)	2449(3)	−411(7)	5744(3)
C(1)	1513(3)	1672(7)	2993(4)
C(2)	1805(3)	897(7)	3904(4)
C(3)	2521(3)	9(8)	4450(4)
C(4)	2804(4)	−591(9)	5340(4)
C(5)	1779(3)	405(7)	5243(4)
C(6)	1415(3)	1072(7)	4300(4)
C(7)	2933(4)	−403(11)	4030(5)
C(8)	1395(5)	599(11)	5707(5)
C(9)	661(4)	3090(9)	1500(5)
C(101)	791(9)	5065(21)	1646(12)
C(111)	222(14)	5846(23)	1712(16)
C(102)	220(12)	4774(22)	1208(12)
C(112)	729(14)	6165(26)	1949(14)
C(12)	259(9)	7866(12)	1630(11)

TABLE II. Fractional Atomic Coordinates (×10^3) for the Hydrogen Atoms with e.s.d.s in Parentheses.

	x/a	y/b	z/c
H(1)	237(3)	−263(8)	342(4)
H(2)	186(3)	172(6)	285(3)
H(3)	327(3)	−122(7)	571(4)
H(4)	301(3)	55(8)	372(4)
H(5)	341(4)	−75(8)	454(4)
H(6)	116(3)	158(9)	562(4)
H(7)	174(4)	15(8)	644(5)
H(8)	94(4)	−28(8)	541(4)
H(9)	17(3)	254(8)	84(4)
H(10)	110(3)	285(7)	150(4)
H(111)	135(7)	543(16)	230(8)
H(121)	63(6)	587(14)	98(8)
H(131)	−29(11)	520(26)	110(13)
H(141)	29	551	228
H(112)	−26(10)	444(21)	115(11)
H(122)	4(7)	532(16)	50(9)
H(132)	90	569	271
H(142)	132(9)	606(20)	202(11)
H(15)	−21(5)	805(12)	150(6)
H(16)	2(5)	814(12)	85(6)
H(17)	67(5)	844(12)	217(6)

TABLE III. Thermal Parameters (×10^4 for Cu, O, N, C and ×10^3 for H) with e.s.d.s in Parentheses. Anisotropic Thermal Parameters are in the Form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})]$.

Atom	U11	U22	U33	U23	U13	U12
Cu	409(5)	358(5)	448(5)	0	278(4)	0
O(1)	456(21)	566(27)	493(22)	47(20)	300(19)	40(20)
O(2)	643(27)	666(32)	595(27)	104(24)	392(24)	107(24)
N(1)	475(26)	343(24)	483(25)	−12(21)	317(22)	−16(21)
N(2)	536(31)	529(33)	485(29)	39(26)	233(26)	42(26)
C(1)	407(32)	399(31)	554(33)	−50(25)	318(28)	−61(24)
C(2)	377(28)	348(30)	477(31)	−18(26)	230(26)	−13(23)
C(3)	411(31)	459(35)	570(39)	−44(30)	267(30)	−46(26)
C(4)	422(34)	570(39)	543(37)	39(33)	186(30)	80(32)
C(5)	479(33)	423(32)	448(33)	−41(27)	250(28)	−64(27)
C(6)	377(29)	353(31)	438(31)	−45(25)	194(26)	−30(24)
C(7)	460(39)	773(51)	675(47)	87(41)	325(38)	112(37)
C(8)	750(49)	661(50)	563(43)	55(40)	413(40)	50(45)
C(9)	635(43)	532(38)	585(38)	105(33)	426(36)	85(35)
C(101)	544(97)	456(86)	532(81)	116(68)	232(79)	16(70)
C(111)	927(147)	635(100)	816(141)	−78(94)	619(138)	−119(101)
C(102)	522(121)	634(111)	476(95)	129(86)	237(93)	−37(92)
C(112)	662(146)	514(120)	884(128)	−3(98)	399(123)	−64(114)
C(12)	1276(108)	528(46)	1590(120)	69(66)	833(100)	160(63)

Atom	U	Atom	U	Atom	U	Atom	U
H(1)	97(19)	H(7)	96(19)	H(121)	40(30)	H(132)	78
H(2)	47(14)	H(8)	110(19)	H(131)	57(63)	H(142)	131(45)
H(3)	65(16)	H(9)	73(17)	H(141)	85	H(15)	121(34)
H(4)	71(19)	H(10)	84(16)	H(112)	123(52)	H(16)	180(36)
H(5)	68(19)	H(111)	68(32)	H(122)	55(36)	H(17)	181(36)
H(6)	102(20)						

TABLE IV. Bond Distances (Å) and Angles (°) with e.s.d.s.

Cu–O(1)	1.900(4)	O(2)–H(1)	1.00(7)
Cu–N(1)	1.981(6)	C(1)–H(2)	0.94(8)
O(1)–C(6)	1.304(7)	C(4)–H(3)	0.94(5)
N(1)–C(1)	1.282(6)	C(7)–H(4)	1.00(7)
C(1)–C(2)	1.442(9)	C(7)–H(5)	0.90(6)
C(2)–C(3)	1.420(8)	C(8)–H(6)	0.88(7)
C(3)–C(4)	1.363(10)	C(8)–H(7)	1.08(7)
C(4)–N(2)	1.349(13)	C(8)–H(8)	1.05(7)
N(2)–C(5)	1.323(8)	C(9)–H(9)	1.07(5)
C(5)–C(6)	1.424(9)	C(9)–H(10)	0.98(8)
C(6)–C(2)	1.406(12)	C(101)–H(111)	1.08(10)
C(3)–C(7)	1.515(14)	C(101)–H(121)	1.18(14)
C(7)–O(2)	1.417(9)	C(111)–H(131)	1.09(16)
C(5)–C(8)	1.501(15)	C(111)–H(141)	0.95
N(1)–C(9)	1.481(11)	C(102)–H(112)	1.03(24)
C(9)–C(101)	1.56(2)	C(102)–H(122)	1.13(16)
C(101)–C(111)	1.46(4)	C(112)–H(132)	1.21
C(111)–C(12)	1.59(2)	C(112)–H(142)	1.23(23)
C(9)–C(102)	1.52(2)	C(12)–H(15)	0.92(12)
C(102)–C(112)	1.53(2)	C(12)–H(16)	1.15(10)
C(112)–C(12)	1.56(3)	C(12)–H(17)	0.93(7)

O(1)–Cu–N(1)	90.7(2)	C(3)–C(4)–N(2)	124.6(8)
O(1)–Cu–O(1^{i})	167.2(2)	C(4)–N(2)–C(5)	117.9(5)
O(1)–Cu–N(1^{i})	90.4(2)	N(2)–C(5)–C(6)	123.2(7)
N(1)–Cu–N(1^{i})	170.5(2)	C(5)–C(6)–C(2)	117.8(7)
Cu–O(1)–C(6)	125.4(4)	C(2)–C(3)–C(7)	121.3(6)
Cu–N(1)–C(1)	123.4(4)	C(4)–C(3)–C(7)	120.1(7)
Cu–N(1)–C(9)	119.3(5)	N(2)–C(5)–C(8)	117.0(6)
C(1)–N(1)–C(9)	117.1(6)	C(6)–C(5)–C(8)	119.8(6)
O(1)–C(6)–C(2)	124.1(5)	C(3)–C(7)–O(2)	112.9(6)
O(1)–C(6)–C(5)	118.2(7)	N(1)–C(9)–C(101)	110.0(8)
N(1)–C(1)–C(2)	125.9(7)	C(9)–C(101)–C(111)	110.2(1.5)
C(1)–C(2)–C(3)	120.3(6)	C(101)–C(111)–C(12)	108.2(2.3)
C(1)–C(2)–C(6)	121.4(6)	N(1)–C(9)–C(102)	114.7(1.0)
C(6)–C(2)–C(3)	118.2(5)	C(9)–C(102)–C(112)	110.2(1.5)
C(2)–C(3)–C(4)	118.4(7)	C(102)–C(112)–C(12)	108.8(1.6)

Key to symmetry operation (i) $\bar{x}, y, \frac{1}{2} - z$

scale was established by Wilson's method. No correction for absorption was applied because of the low value of μR.

Structure Determination and Refinement

The structure was solved by the heavy-atom method locating the Cu atom. Successive Fourier syntheses revealed the positions of all other non-hydrogen atoms and the disordered distribution of the two central atoms of the n-butyl chain. The refinement was carried out by least-squares full-matrix cycles using the SHELX system of computer programs [7] with initially isotropic and then anisotropic thermal parameters. The site occupancy factors of the two disordered C atoms were also refined and a fifty-fifty distribution was found. The positions of all the hydrogen atoms (and surprisingly even those of the disordered C) were determined by difference Fourier syntheses. At this stage a final least-squares cycle was computed, including the H atoms with isotropic thermal parameters (only H141 and H132 were fixed). The best results were obtained using unit weights giving a final conventional $R(F)$ = 0.0377 (observed reflections only). Scattering factors for Cu^{2+}, C, H, N and O were taken from the International Tables for X-ray Crystallography [8], as were the real and imaginary parts of the anomalous scattering [9]. Final atomic coordinates for non-hydrogen and for hydrogen atoms are given in Table I and Table II respectively. The thermal parameters are given in Table III. A list of observed and calculated structure factors is available from the authors on request.

TABLE V. Weighted Least-squares Planes[a] and Lines[b] with Deviations (Å) and e.s.d.s of the Relevant Atoms in Squares Brackets. Angles (°) between Some Significative Planes, Plane and Line, and between Lines.

		M1	M2	M3	D
Plane 1	O(1), N(1), O(1^{i}), N(1^{i}) [O(1) +0.156(4), N(1) −0.221(5), O(1^{i}) +0.156(4), N(1^{i}) −0.221(5), Cu −0.056(1)]	0	−1	0	−1.55966
Plane 2	Cu, O(1), N(1)	−0.07248	0.99040	0.11767	2.20490
Plane 3	N(1), C(1), C(2), C(6), O(1) [N(1) +0.035(5), C(1) −0.076(6), C(2) + 0.042(6), C(6) +0.010(6), O(1) −0.014(4), Cu +0.580(1)]	−0.23778	−0.88701	−0.39581	−2.74051
Plane 4	N(1), C(1), C(2), C(6) [N(1) +0.020(5), C(1) −0.057(6), C(2) +0.053(6), C(6) −0.025(6), O(1) −0.089(4), Cu +0.498(1)]	−0.20266	−0.89565	−0.39591	−2.76776
Plane 5	N(2), C(5), C(6), C(2), C(3), C(4) [N(2) −0.001(6), C(5) −0.007(6), C(6) +0.012(6), C(2) −0.010(6), C(3) +0.004(6), C(4) +0.004(7), C(1) −0.118(6), C(7) +0.134(9), C(8) −0.018(9), O(1) +0.051(4), H(3) +0.04(6)]	−0.28298	−0.86831	−0.40739	−2.72564
Plane 6	O(1), C(6), C(2), C(1), N(1), C(3), C(4), N(2), C(5) [O(1) +0.008(4), C(6) −0.007(6), C(2) +0.001(6), C(1) −0.101(6), N(1) +0.046(5), C(3) +0.039(6), C(4) +0.033(7), N(2) −0.000(6), C(5) −0.029(6), Cu +0.634(1)]	−0.26142	−0.87430	−0.40896	−2.75500

		X_0	Y_0	Z_0	M1	M2	M3
Line A	H(1)N(2^{ii})	1.24682	−2.81108	5.32050	−0.25677	−0.76961	0.58461
Line B	C(2^{ii})N(2^{ii})	0.70224	−4.08325	7.17532	−0.20666	−0.36287	0.90863
Line C	C(4)C(4^{ii})	0.07290	−1.94700	6.93134	−0.18868	−0.93612	−0.29677

Angles (°) involving planes and lines

2–2^{i}	15.9(2)	2–3	155.2(2)	3–5	2.9(2)	6–6^{i}	121.9(1)	5–*C*	80.8(2)	*A*–*B*	30.3(3)

[a] The equations are in the form M1X + M2Y +M3Z = D, where X, Y, Z are orthogonal coordinates (in Å) measured along *a*, *b*, and *c**. [b] The equations are in the form X − X_0/M1 = Y − Y_0/M2 = Z − Z_0/M3, where M1, M2, M3 are the direction cosines referred to the X, Y, Z orthogonal axes; X_0, Y_0, Z_0 are the coordinates of the centroid of the set of atoms.
(*i*) $\bar{x}, y, \frac{1}{2} - z$ (*ii*) $\frac{1}{2} - x, -\frac{1}{2} - y, 1 - z$

All the calculations were carried out on the CYBER 76 computer of the 'Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna)', with the financial support of the University of Parma.

Results and Discussion

The structure and atom numbering scheme of the complex is shown in Fig. 1. Bond distances involving all the atoms and angles for the non-hydrogen ones are given in Table IV. The Cu atom lies on a crystallographic two-fold axis and is chelated to two pyridoxylidene ligands through the two imino nitrogen and the two phenolate oxygen atoms in a *trans*-configuration. Coordination around the metal is not strictly planar but shows tetrahedral displacements: O(1) and N(1) are + 0.156(4), −0.221(5) Å respectively out of the weighted least-squares plane through the four coordinated atoms; Cu is −0.056(1) Å out of sample plane (Table V). The angles between the O and N co-ordinating atoms are very flattened and some different [O(1)–Cu–O(1^{i}) = 167.2(2) and N(1)–Cu–N(1^{i}) = 170.5(2)°, $i = \bar{x}, y, \frac{1}{2} - z$]. One of the best direct measures of the degree of distortion is the dihedral angle [θ = 15.9(2)°] between the Cu, O(1), N(1) and Cu, O(1^{i}), N(1^{i}) planes. The Cu–O(1) and Cu–N(1) distances [1.900(4), 1.981(6) Å] agree with the values found in similar bis(N-R-salicylideneiminato)Cu(II) complexes [10]. There are

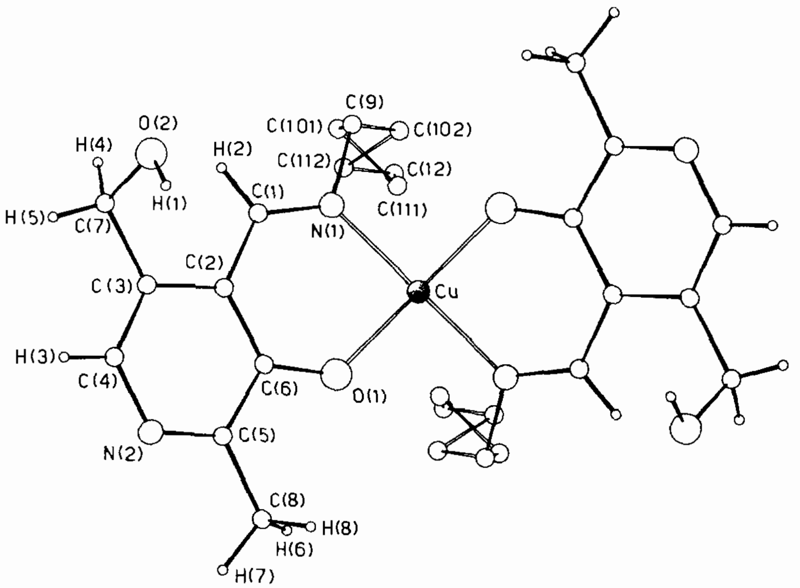

Fig. 1. Projection of the complex along the twofold axis.

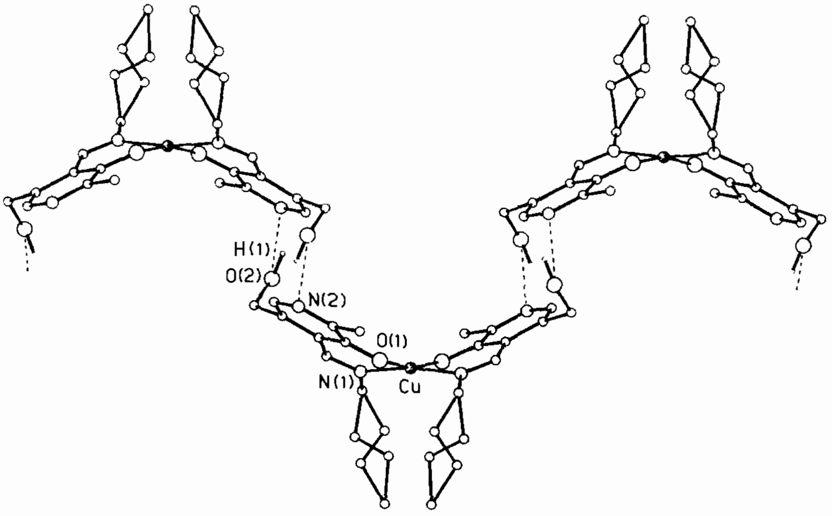

Fig. 2. Perspective view of the polymeric chain running parallel to [101].

no significant differences between the 'bite' [O(1)$\cdots$N(1) = 2.761(9) Å] and 'non-bite' [O(1)$\cdots$N(1^i) = 2.754(5) Å] distances in the coordination polyhedron, even if there is a short interaction between O(1) and the first C atom of the n-butyl substituted imine [O(1)$\cdots$C(9^i) = 2.921(11) Å].

There is a considerable bending along the 'bite' of the ligand. The dihedral angle between the mean planes passing through Cu, O(1), N(1) and N(1), C(1), C(2), C(6), O(1) is 155.2(2)°. The Cu atom is significantly out of this latter plane by 0.580(1) Å. The chelate ring conformation is intermediate between the half-chair and the sofa one: ΔC_2(C(1)—C(2)) = 9° and ΔC_s(Cu) = 12° [11]. The angle of tilt between the mean planes of the pyridine and chelate rings is only 2.9(2)°. With respect to the coordination polyhedron the two pyridoxylidene moieties are tipped in the same direction giving a butterfly effect to the molecular skeleton, thus forming a dihedral angle of 121.9(1)° (Fig. 2). In the analogous complex with the salicylaldehyde [12], Cu(II) being on a centre of symmetry, the two benzene rings are parallel with a step of 0.74 Å. Bond distances and angles in the pyridoxylidene moiety are in good agreement with those found in other compounds containing the same moiety. The C(4)—

TABLE VI. Selected Torsion Angles (°) with e.s.d.s.

Cu–O(1)–C(6)–C(2)	23(1)
O(1)–C(6)–C(2)–C(1)	6(1)
C(6)–C(2)–C(1)–N(1)	−14(1)
C(2)–C(1)–N(1)–Cu	−6(1)
C(1)–N(1)–Cu–O(1)	24(1)
N(1)–Cu–O(1)–C(6)	−32(1)
N(2)–C(5)–C(8)–H(6)	141(5)
N(2)–C(5)–C(8)–H(7)	6(5)
N(2)–C(5)–C(8)–H(8)	−103(4)
C(6)–C(5)–C(8)–H(6)	−39(5)
C(6)–C(5)–C(8)–H(7)	−175(5)
C(6)–C(5)–C(8)–H(8)	76(4)
C(2)–C(3)–C(7)–O(2)	−65(1)
C(2)–C(3)–C(7)–H(4)	50(4)
C(2)–C(3)–C(7)–H(5)	168(5)
C(4)–C(3)–C(7)–O(2)	110(1)
C(4)–C(3)–C(7)–H(4)	−135(4)
C(4)–C(3)–C(7)–H(5)	−17(5)
C(3)–C(7)–O(2)–H(1)	−53(4)
H(4)–C(7)–O(2)–H(1)	−178(6)
H(5)–C(7)–O(2)–H(1)	68(7)
C(1)–N(1)–C(9)–C(101)	−95(1)
N(1)–C(9)–C(101)–C(111)	−67(2)
C(9)–C(101)–C(111)–C(12)	−168(1)
C(1)–N(1)–C(9)–C(102)	−136(1)
N(1)–C(9)–C(102)–C(112)	68(2)
C(9)–C(102)–C(112)–C(12)	−180(2)

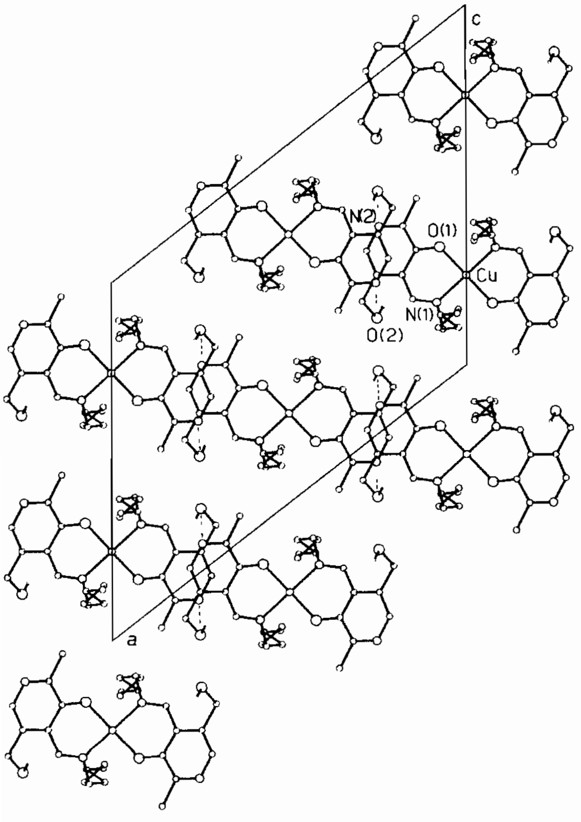

Fig. 3. Projection of the structure along *b*.

TABLE VII. Intra- and Intermolecular Contacts with e.s.d.s.

a) *Significative bond distances* (Å) *and angles* (°) *for the hydrogen bond*

O(2)···N(2^{ii})	2.920(8)
H(1)···N(2^{ii})	1 98(7)
O(2)–H(1)···N(2^{ii})	155(12)
H(1)–O(2)···N(2^{ii})	17(8)
O(2)···N(2^{ii})–C(4^{ii})	115.5(9)
O(2)···N(2^{ii})–C(5^{ii})	113.1(7)
H(1)···N(2^{ii})–C(4^{ii})	113(7)
H(1)···N(2^{ii})–C(5^{ii})	120(6)

b) *Selected interactions* (Å)

O(2)···C(1)	3.199(8)
O(2)···C(2)	3.117(10)
N(1)···C(111)	2.987(19)
N(1)···C(112)	3.087(21)
C(1)···C(101)	3.238(17)
O(1)···C(9^{i})	2.921(11)
O(1)···C(102^{i})	3.089(24)
C(4)···C(4^{ii})	3.176(10)

Key to symmetry operations

(*i*) $\bar{x}, y, \frac{1}{2} - z$
(*ii*) $\frac{1}{2} - x, -\frac{1}{2} - y, 1 - z$

N(2)–C(5) angle of the pyridine ring is significantly less than 120° and is characteristic for a deprotonated nitrogen. The H(7) atom of the methyl group lies roughly in the pyridine plane (Table VI). The C(3), C(7), O(2), H(1) fragment adopts an helicoidal geometry. In fact both the oxygen and the hydrogen of the alcoholic group are synclinal with regard to C(2) and C(3) respectively; O(2) so forms two weak interactions with C(1) and C(2) (Table VII). Although the antiperiplanar conformation should be the most favourable to yield the minimum hindrance, the synclinal one is realized in order to form an intermolecular hydrogen bond involving the pyridinic N. This type of hydrogen bond is rather weak (Table VII); in spite of the fairly good angle values, the hydrogen and the oxygen of alcoholic group deviate 1.00(6) and 1.760(5) Å from the(*iii*) pyridinic plane (*ii* = ½ − *x*, −½ −*y*, 1 − *z*). H(1) and O(2) atoms line up symmetrically with respect to C(4^{ii}) and C(5^{ii}). Even if it is not strictly correct from a geometrical point of view, another way to quantify the distortion of this hydrogen bond is the angle value between the line H(1)N(2^{ii}) and the approximate direction of the lone-pair $C(2^{ii})N(2^{ii})$: 30.3(3)°.

Packing is determined by the above-mentioned hydrogen bonds which form strip-like chains running parallel to [101] (Fig. 3). An additional interesting interaction $C(4)\cdots C(4^{ii})$ = 3.176(10) Å occurs in the zig-zag chain between adjacent pyridine rings related by an inversion center in such a way that the $C(4)C(4^{ii})$ line is quite perpendicular to the relative aromatic rings having a step of 3.144(23) Å. These strips are held together by weak Van der Waals contacts, all greater than 3.5 Å.

The n-butyl chain is statistically distributed with a fifty-fifty occupancy factor for the two central C atoms and adopts an extended form. Nevertheless the imino nitrogen does not lie in either alkyl group plane. C(111) and C(112) are –synclinal and +synclinal with respect to N(1). This type of conformation causes some short interactions between C(102) and $O(1^{i})$, C(1) and C(101), N(1) and C(111) and between N(1) and C(112). In bis(N-n-butylsalicylideneiminato)copper(II) the alkyl group adopts the synclinal conformation while the last C but one is antiperiplanar with respect to the imino N.

Extensive use of the Cambridge Crystallographic Data Files has been made for the bibliography search.

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