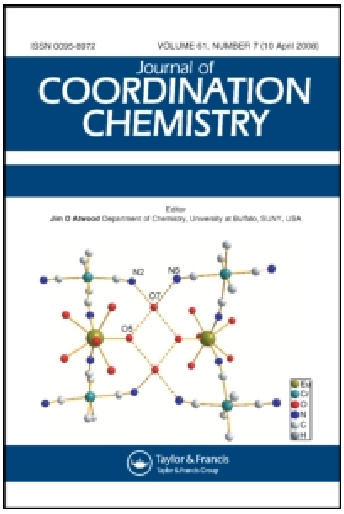

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SPECTROSCOPIC AND X-RAY STRUCTURAL STUDY OF THE COPPER(II) COMPLEX WITH SCHIFF BASE BETWEEN PYRIDOXAL AND BENZYLAMINE

Françoise Nepveu[a]; Jean-Jacques Bonnet[a]; Jean-Pierre Laurent[ab]; Michel Massol[c]
[a] Laboratoire de Chimie de Coordination du CNRS, Toulouse, France [b] Associated to the University Paul Sabatier, Toulouse, France [c] Laboratoire de Chimie Bioinorganique 38, Toulouse, France

To cite this Article Nepveu, Françoise , Bonnet, Jean-Jacques , Laurent, Jean-Pierre and Massol, Michel(1981) 'SPECTROSCOPIC AND X-RAY STRUCTURAL STUDY OF THE COPPER(II) COMPLEX WITH SCHIFF BASE BETWEEN PYRIDOXAL AND BENZYLAMINE', Journal of Coordination Chemistry, 11: 3, 185 — 193

To link to this Article: DOI: 10.1080/00958978108079068
URL: http://dx.doi.org/10.1080/00958978108079068

J. Coord. Chem., 1981, Vol. 11, 185–193
0095-8972/81/1103-0185 $06.50/0

SPECTROSCOPIC AND X-RAY STRUCTURAL STUDY OF THE COPPER(II) COMPLEX WITH SCHIFF BASE BETWEEN PYRIDOXAL AND BENZYLAMINE

FRANÇOISE NEPVEU, JEAN-JACQUES BONNET and JEAN-PIERRE LAURENT

Laboratoire de Chimie de Coordination du CNRS†, *205, Route de Narbonne, 31400 Toulouse, France*

and

MICHEL MASSOL

Laboratoire de Chimie Bioinorganique 38, rue des 36 Ponts, 31400 Toulouse, France

(*Received May 21, 1981*)

Bis(*N*-benzylpyridoxaldiminato) copper(II) has been prepared and studied in solution and solid state. The complex crystallizes in the monoclinic space group $C^5_{2h} - P2_1/a$ in a cell of a = .9561(9), b = 16.605(8), c = 17.561(2) Å and β = 104.14(1). Based on 3684 unique reflections, the structure was refined by fullmatrix least-squares techniques to a conventional agreement factor (on F) of R = 0.045. Each ligand is bidentate through the phenolic oxygen and the imino nitrogen atoms, leading to a tetrahedrally distorted square planar environment about the copper atom. The dihedral angle between the two chelating moieties is 35.31°. The two benzyl groups are, surprisingly, in a *cis* position with respect to the mean plane of the molecule. In solution, the ESR data are consistent with a distorted square planar structure around Cu. Under particular conditions two sets of ESR signal are observed, suggesting the occurrence of two species.

INTRODUCTION

Among the variety of enzymatic reactions which are catalyzed by pyridoxal (the aldehydic form of vitamin B_6) we have focused our attention on the possible role of this cofactor, jointly with copper(II) ion, in the oxydative deamination reactions.[1-3] Nonenzymatic model reactions involving amino-acids have been considered[4] and they have emphasized the complementary roles of pyridoxal and of a suitable metal ion. In this instance, transition metal complexes of Schiff bases derived from pyridoxal and amino-acids have been extensively investigated for many years.[5-8] In contrast, the Schiff base complexes derived from pyridoxal and amines are less well-known. Furthermore, no model system yet investigated clearly establishes that the mechanisms operative in the case of amino-acids may be extented to biogenic amines. In order to develop a better understanding of these mechanisms we have undertaken an investigation of the Schiff base copper(II) complexes obtained from pyridoxal and biogenic amines.[11]

The present paper reports the preparation and characterization of the Schiff base copper(II) complex obtained from pyridoxal and benzylamine. The occurence of two isomers in solution is discussed in relation with the results of X-ray structural determination and ESR spectra.

EXPERIMENTAL

Materials and Methods

Pyridoxal hydrochloride (PL) (Sigma Chemical Co) and benzylamine (ByA) (Fluka) were used without further purification.

Conductance measurements were carried out at 25°C using a Beckmann RC 18 conductance bridge. Infrared spectra in KBr pellets were recorded on a Perkin Elmer Model 577 spectrophotometer. ^1H NMR spectra were recorded on a WH 90 Brucker

---

†Associated to the University Paul Sabatier, Toulouse, France

spectrophotometer. The chemical shifts are given in parts per million downfield from tetramethylsilane (internal standard). Visible spectra were obtained with a Cary Model 14 recording spectrophotometer. The magnetic measurements were carried out with a Faraday-type magnetometer at room temperature, mercurytetrathiocyanatocobaltate(II) being used as susceptibility standard. The magnetic susceptibility was corrected for the diamagnetic contribution of the ligand. ESR spectra were recorded on a Brucker ER 200 D spectrometer operating at X-band. Spectra were calibrated using diphenylpicrylhydrazyl (dpph, g = 2.0036) as a field marker.

Preparation

N-benzylpyridoxaldimine: the Schiff base was prepared by adding pyridoxal hydrochloride (0.51 g, 2.5 mmole) to a solution of benzylamine (0.27 g, 2.5 mmole) in 25 ml of pentane. The mixture was refluxed for 30 mn. The resulting yellow precipitate was collected by filtration and dried under vacuum. ^{1}H NMR : δ9.05 (C$\underline{H}$ = N(PL)), 7.85 (C$\underline{H}$ = (PL)), 7.35 ($C_6\underline{H}_5$(ByA)), 4.88 (C$\underline{H}_2$(ByA)), 4.77 (C$\underline{H}_2$OH(PL)), 2.43 (C$\underline{H}_3$(PL)) ppm in CD_3OD.

Bis(*N*-benzylpyridoxaldiminato)copper(II) complex: to a solution of benzylamine (0.54 g, 5 mmole) dissolved in 30 ml of ethanol, were added pyridoxal hydrochloride (1.02 g, 5 mmole) and sodium acetate (0.68 g, 5 mmole); after stirring (20 mn), copper acetate (0.5 g, 2.5 mmole) was added and the resulting mixture was refluxed for two hours and then reduced to a volume of about 5 ml. Salts were precipitated by adding isopropanol (30 ml) and removed by filtration. Evaporation of the filtrate to a volume of about 5 ml and addition of 50 ml of hexane led to precipitation of the product (1.29 g, 90% yield). Final purification was achieved by column chromatography on 70–230 mesh silicagel (60 Merck Kiesielgel) with a methanol/acetone mixture (80 : 20, V/V) as eluant. From the collected phase, dark green parallelepipedic crystals were obtained by slow evaporation : Anal. Calcd for $C_{30}H_{30}N_4O_4Cu$: C, 62.75; H, 5.26; N, 9.75; Cu, 11.06. Found : C, 62.72; H, 5.21, N, 9.49; Cu, 10.83. M.P. 163–164°. Λ = 4.7 ohm^{-1} cm^2 mole^{-1} (10^{-3} M in methanol). μ = 1.90 BM.

Collection and Reduction of the X-ray Data

Preliminary photographic data revealed that crystals of the complex belong to the monoclinic system and show systematic extinctions (0*k*0, *k* = 2*n* + 1 and *h*01, *h* = 2*n* + 1) consistent with the space groupe $P2_1/a$.

Cell constants and corresponding standard deviations

TABLE I
Summary of crystal data and intensity collection.

Compound	$(N(-C_7H_5)C_8H_{10}N_2O_2)_2Cu$
Formula	$C_{30}H_{30}N_4O_4Cu$
Formula weight	574.14 amu
a (at 20°C)	9.561 (9) Å
b	16.605 (8) Å
c	17.561 (2) Å
β	104.14 (1)°
V	2704 Å^3
Z	4
Density calcd	1.41 g. cm^{-3}
Density (measured at 20°C in aqueous $ZnCl_2$)	1.39 g. cm^{-3}
Space group	C^5_{2h} – $P2_1/a$
Radiation	MoK_α from graphite monochromator ($\lambda(MoK_{\alpha 1})$ = 0.7093 Å)
Linear absorption coefficient	8.5 cm^{-1}
Receiving aperture	3.5 × 4.0 mm; 27 cm from crystal
Take-off angle	2.95°
Values determining the scan speed[13]	
SIGPRE* = 0.66 SIGMA* = 0.018 VPRE* = 4 TMAX* = 60s	
Scan range	0.6° below $K_{\alpha 1}$ to 0.6° above $K_{\alpha 2}$
2θ limits	3–52
Final no. of variables	268
Unique data used	3684
$R = \Sigma\|\|k\,Fo\| - \|Fc\|\|/\Sigma k\|Fo\|$	= 0.045
$R_w = (\Sigma\omega(\|k\,Fo\| - \|Fc\|)^2/\Sigma\omega k^2\|Fo\|^2)^{1/2}$	= 0.053

at 20°C were obtained from a least squares refinement of 25 reflections automatically centered on a CAD4-Enraf-Nonius diffractometer.

The cell constants and other pertinent data are presented in Table I. A total of 5295 intensities were recorded at 20°C out to 2θ(Mo) = 52°. After data processing,[12] only those 3684 unique reflections having $Fo^2 > 3\sigma(Fo^2)$ were used in subsequent calculations.

Solution and Refinement of the Structure

The structure has been solved by standard Patterson and Fourier methods. Conditions of refinement and the indices R and R_w are defined in Table I.

Atomic scattering factors for the nonhydrogen atoms were taken from the usual tabulation[14] whereas the hydrogen atom scattering factors used were those of Stewart *et al.*[15] Anomalous dispersion terms for the Cu atom were included in Fc.[16]

Refinement of an isotropic model converged to values of R and R_w of 0.075 and 0.0980. a difference Fourier map clearly revealed the positons of 28 among the 30 H atoms. Their contributions to Fc from idealized positions[12] were calculated and then used in subsequent cycles of refinement. For each hydrogen atom, an isotropic thermal parameter was assigned with a value 1.0Å^2 greater than of the C atom to is attached.

Carbon atoms in phenyl groups were constrained to D_{6h} geometry (C—C = 1.395 Å), an isotropic thermal parameter being assigned for each of them.

The last cycle of refinement included anisotropic thermal parameters for all but hydrogen atoms and carbon atoms of phenyl groups. During this last cycle of refinement, each of all parameter shifts was less than the associated standard deviation.

The final difference Fourier map shows peaks of the order 0.6 (2) e/Å^3 with a random distribution. These peaks are approximately 10% of the heights of typical light atom peaks on earlier Fourier maps. Thus the final difference Fourier map is essentially featureless.

Final non hydrogen parameters are listed in Table II and Table III. Hydrogen atom parameters are given in Table IV. Table V lists the value of 1 Fo/vs.Fc.[17] Table VI contains the root-mean square amplitudes of vibration.

TABLE II
Positional and thermal parameters for the non-group atoms of bis(*N*-benzylpyridoxaldiminato)copper(II)

Atom	A	Y	Z	B11	B22	B33	B12	B13	B23
CU	0.07621(5)	0.01942(3)	0.70004(3)	64.9(5)	17.3(2)	17.9(2)	1.8(3)	5.8(2)	−2.8(2)
O(1)	0.0704(3)	0.1266(1)	0.7369(1)	91.(4)	16.1(10)	19.1(9)	5.(1)	1.(1)	−2.9(8)
O(2)	0.1411(3)	−0.0639(2)	0.6428(a)	72.(3)	27.(1)	23.(1)	8.(2)	5.(1)	−8.5(9)
O(3)	0.5526(3)	0.0951(2)	0.9649(2)	78.(4)	26.(1)	31.(1)	3.(2)	5.(2)	4.3(9)
O(4)	−0.3929(3)	−0.1242(2)	0.4648(2)	82.(4)	31.(1)	41.(1)	−8.(2)	15.(2)	3.(1)
N(1)	0.2044(3)	−0.0153(2)	0.8001(2)	66.(4)	14.(1)	21.(1)	1.(2)	10.(2)	−1.(1)
N(2)	−0.1094(3)	0.0293(2)	0.6223(2)	63.(4)	18.(1)	17.(1)	0.(2)	12.(2)	−0.2(9)
N(3)	0.1639(3)	0.2751(2)	0.8872(2)	96.(5)	20.(1)	23.(1)	1.(2)	9.(2)	−6.(1)
N(4)	0.0740(4)	−0.2088(2)	0.4878(2)	109.(5)	25.(1)	24.(1)	2.(2)	18.(2)	−6.(1)
C(1)	0.1381(4)	0.1573(2)	0.8045(2)	62.(5)	18.(1)	18.(1)	−4.(2)	11.(2)	−1.(1)
C(2)	0.2413(4)	0.1165(2)	0.8620(2)	59.(4)	17.(1)	20.(1)	−5.(2)	11.(2)	−1.(1)
C(3)	0.2646(4)	0.0308(2)	0.8571(2)	62.(4)	19.(2)	19.(1)	−1.(2)	9(2)	0.(1)
C(4)	0.3136(4)	0.1593(2)	0.9305(2)	74.(5)	22.(2)	18.(1)	−5.(2)	10.(2)	0.(1)
C(5)	0.2716(4)	0.2364(2)	0.9389(2)	104.(6)	22.(2)	22.(1)	−6.(2)	7.(2)	−7.(1)
C(6)	0.1016(4)	0.2379(2)	0.8214(2)	74.(5)	17.(1)	23.(1)	−2.(2)	11.(2)	−2.(1)
C(7)	−0.0131(5)	0.2820(2)	0.7624(2)	101.(6)	21.(2)	33.(2)	14.(2)	6.(3)	−2.(1)
C(8)	0.4346(5)	0.1226(2)	0.9926(2)	106.(6)	27.(2)	19.(1)	−6.(3)	1.(2)	−2.(1)
C(9)	0.2200(4)	−0.1031(2)	0.8147(2)	84.(5)	15.(1)	27.(2)	6.(2)	4.(2)	1.(1)
C(10)	−0.1507(4)	−0.0161(2)	0.5617(2)	66.(4)	21.(1)	18.(1)	−5.(2)	7.(2)	3.(1)
C(11)	−0.0707(4)	−0.0803(2)	0.5375(2)	73.(5)	17.(1)	18.(1)	−5.(2)	13.(2)	0.(1)
C(12)	0.0697(4)	−0.1007(2)	0.5792(2)	82.(5)	21.(1)	18.(1)	−1.(2)	17.(2)	−1.(1)
C(13)	−0.1359(4)	−0.1257(2)	0.4699(2)	80.(5)	20.(2)	18.(1)	−10.(2)	11.(2)	0.(1)
C(14)	−0.0604(5)	−0.1878(2)	0.4490(2)	111.(6)	24.(2)	22.(1)	−14.(3)	14.(2)	−7.(1)
C(15)	0.1390(4)	−0.1662(2)	0.5506(2)	97.(6)	24.(2)	23.(2)	5.(3)	14.(2)	−3.(1)
C(16)	0.2900(5)	−0.1888(3)	0.5912(3)	126.(7)	45.(2)	41.(2)	33.(3)	5(3)	−16.(2)
C(17)	−0.2877(4)	−0.1094(3)	0.4224(2)	99.(6)	27.(2)	24.(2)	−8.(3)	3.(2)	−4.(1)
C(18)	−0.2175(4)	0.0865(2)	0.6385(2)	73.(5)	20.(2)	22.(1)	10.(2)	7.(2)	0.(1)

Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. The form of the anisotropic thermal ellipsoid iso exp -($B11H^2 + B22K^2 + B33L^2 + 2B12HK + 2B13HL + 2B23KL$). The quantities given in the table are the thermal coefficients × 10^4.

TABLE III

Derived parameters for the rigid group atoms of bis(N-benzylpyridoxaldiminato)copper(II).

ATOM	X	Y	Z	$B(A^2)$	ATOM	X	Y	Z	$B(A^2)$
C(19)	0.0832(3)	−0.1330(2)	0.8323(2)	2.95(8)	C(25)	−0.2856(3)	0.0505(2)	0.6987(1)	2.42(7)
C(20)	0.0634(3)	−0.1233(2)	0.9077(1)	3.96(2)	C(26)	−0.4071(3)	0.0020(2)	0.6744(1)	3.71(9)
C(21)	−0.0645(4)	−0.1484(2)	0.9247(1)	5.2(1)	C(27)	−0.4691(3)	−0.0340(2)	0.7297(2)	4.6(1)
C(22)	−0.1727(3)	−0.1832(2)	0.8663(2)	5.5(1)	C(28)	−0.4097(3)	−0.0216(2)	0.8095(2)	4.48(10)
C(23)	−0.1529(3)	−0.1929(2)	0.7910(2)	5.8(1)	C(29)	−0.2882(3)	0.0268(2)	0.8338(1)	3.99(9)
C(24)	−0.0250(3)	−0.1678(2)	0.7739(1)	4.6(1)	C(30)	−0.2262(2)	0.0629(2)	0.7784(1)	3.59(9)

Rigid group parameters

GROUP	X_C	Y_C	Z_C	DELTA	EPSILON	ETA
PH(1)	−0.0448(2)	−0.1581(1)	0.8493(1)	−0.837(4)	−2.047(2)	1.927(4)
PH(2)	−0.3477(7)	0.0144(1)	0.7541(1)	2.113(2)	2.519(1)	1.727(2)

X_C, Y_C, and Z_C are the fractional coordinates of the origin of the rigid group. The rigid group orientation angles delta. (epsilon. and eta(radians) have been defined previously by S. J. La Placa and J. A. Ibers, *Acta crystallogr.*, **18**, 511) 1965.

TABLE IV

Idealized H parameters (see text).

ATOM	X	Y	Z	$B(Å^2)$
H–C(20)	0.137	0.100	0.948	4.98
H–C(21)	−0.078	−0.142	0.976	6.32
H–C(22)	−0.261	−0.200	0.878	6.49
H–C(23)	−0.227	−0.216	0.751	6.67
H–C(24)	−0.012	−0.175	0.723	5.44
H–C(26)	−0.143	0.096	0.795	4.51
H–C(27)	−0.247	0.035	0.888	4.93
H–C(28)	−0.451	−0.047	0.847	5.55
H–C(29)	−0.551	−0.067	0.713	5.73
H–C(30)	−0.447	−0.006	0.620	4.59
H–O(3)	0.333	0.006	0.901	3.21
H–O(5)	0.321	0.265	0.986	3.81
H–C(14)	−0.107	−0.218	0.402	3.92
H–C(10)	−0.246	−0.006	0.530	3.28
H(1)–C(8)	0.465	0.161	1.033	3.96
H(2)–C(8)	0.394	0.077	1.015	3.96
H(1)–C(9)	0.302	−0.114	0.857	3.65
H(2)–C(9)	0.238	−0.130	0.769	3.65
H(1)–C(17)	−0.294	−0.054	0.406	4.24
H(2)–C(17)	−0.307	−0.142	0.376	4.24
H(1)–C(18)	−0.175	0.137	0.656	3.42
H(2)–C(18)	−0.292	0.096	0.590	3.42
H(1)–C(7)	−0.013	0.338	0.775	4.46
H(2)–C(7)	0.001	0.276	0.710	4.46
H(3)–C(7)	−0.106	0.260	0.762	4.46
H(1)–C(16)	0.309	−0.243	0.577	5.98
H(2)–C(16)	0.356	−0.153	0.577	5.98
H(3)–C(16)	0.302	−0.187	0.647	5.98
H–O(3)	0.632	0.078	0.946	4.23
H–O(4)	−0.463	−0.135	0.493	4.69

TABLE VI

Root-mean square amplitudes of vibration (Å) in bis(*N*-benzylpyridoxaldiminato)copper(II).

ATOM	Min	Int.	Max
Cu	0.145(1)	0.163(1)	0.180(1)
0(1)	0.142(5)	0.162(4)	0.218(4)
0(2)	0.148(5)	0.170(4)	0.230(4)
0(3)	0.172(5)	0.195(4)	0.227(4)
0(4)	0.174(5)	0.214(4)	0.248(4)
N(1)	0.140(5)	0.169(5)	0.178(5)
N(2)	0.150(5)	0.160(6)	0.170(5)
N(3)	0.150(6)	0.196(5)	0.211(5)
N(4)	0.155(6)	0.209(5)	0.220(6)
C(1)	0.150(7)	0.156(7)	0.174(6)
C(2)	0.145(7)	0.162(6)	0.175(6)
C(3)	0.160(7)	0.168(31)	0.169(27)
C(4)	0.159(6)	0.168(6)	0.187(6)
C(5)	0.146(7)	0.201(6)	0.218(6)
C(6)	0.153(7)	0.179(7)	0.188(6)
C(7)	0.154(7)	0.206(6)	0.244(6)
C(8)	0.159(7)	0.195(6)	0.229(6)
C(9)	0.134(7)	0.185(6)	0.215(6)
C(10)	0.150(7)	0.164(6)	0.189(6)
C(11)	0.145(7)	0.158(6)	0.185(6)
C(12)	0.146(7)	0.170(6)	0.194(6)
C(13)	0.151(7)	0.164(6)	0.201(6)
C(14)	0.148(7)	0.190(6)	0.234(6)
C(15)	0.165(7)	0.193(6)	0.210(6)
C(16)	0.164(8)	0.224(6)	0.329(7)
C(17)	0.167(7)	0.206(6)	0.226(6)
C(18)	0.149(7)	0.179(6)	0.200(6)

TABLE VII
ESR Parameters for the copper(II) complex.

Spectrum[a]	Conditions	g_0	Ao (10^4 cm^{-1})	$g_{//}$	$g_{\perp}$	A (10^4 cm^{-1})	$\langle g \rangle$[b]
	1) *Solid state*						
(a)	293 K	2.10	65				
	2) *In solution*						
	– crystallised complex						
(b)	• in MeOH/CH_2Cl_2 (v/v : 1/4) 10^{-3} M; 293 K	2.11					
(b′)	• in MeOH, 10^{-3} M; 293 K	2.13					
(c)	• in MeOH/CH_2Cl_2 (v/v : 1/4) 10^{-3} M; 111 K			2.25	2.04	182	2.11
(c′)	• in MeOH; 10^{-3} M; 98 K			2.24	2.06	181	2.12
	– Solution of ligand (0.1 M) with $CuCl_2$ (0.01 M)						
(d)	• in MeOH, 92 K I			2.26	2.06	183	2.13
	II			2.32	2.06	173	2.15
(d′)	• in MeOH/CH_2Cl_2 (v/v) : 1/4)						
	I			2.26	2.06	183	2.13
	II			2.32	2.06	173	2.15

[a] Spectra corresponding to unprimed letters are given in Figure 1.
[b] Calculated from $\langle g \rangle = (g_{//} + 2g_{\perp})/3$.

RESULTS AND DISCUSSION

Analytical data and conductibility measurements lead to the conclusion that the complex under investigation displays a 1/2 metal to ligand stoichiometry and is a non electrolyte. In this instance the Schiff base actually behaves as a bidentate monobasic ligand. Regarding the metal, the occurence of a copper(II) ion is supported by the characteristic value[18] (1.90 B.M.) of the magnetic moment. As expected, some information on the nature of the coordination sites may be drawn from a consideration of the i.r. spectra. First of all, the two characteristic absorptions which are located at 1628 and 1540 cm^{-1} in the free ligand, suffer down shifts (8 and 17 cm^{-1} respectively) upon complexation. Since they are attributable to ν(C=N) and to ν(C—O) phenolic,[19] their modifications may be connected to a lowering of the multiplicity of these two bonds upon coordination of the ligand through the nitrogen atom of the azomethine group and through the phenolic oxygen. Coordination of the Cu(II) ion to the ligand through the oxygen of the phenolic group and through the nitrogen of the imine group is further supported by the appearance of two sharp bands of medium intensity at 552 and 498 cm^{-1}, which are attributable to ν(Cu—O) and ν(Cu—N).[20]

The main feature of the electronic spectrum is the occurrence of a broad band which is centred at 628 nm (ε = 132 l. mole^{-1} cm^{-1}) in solution and at 630 nm in the solid state (diffuse reflectance spectrum). This band actually appears as a shoulder on the longer wavelength side of a charge transfert absorption. The 628 (or 630) nm absorption is attributable to a ligand-field d → d transition with a $d_{x^2-y^2}$ ground state. The values of its extinction coefficient (ε = 132 l. mole^{-1} cm^{-1}) and of its frequency, which is lower than the values reported[11] for bis(*N*-substituent pyridoxaldiminato) copper(II) complexes, are consistent with some degree of distortion from an ideal square planar environment.[21]

The ESR data related to polycrystalline samples and to solutions are summarized in Table VII (Figure 1). The ESR spectrum of pure solid polycrystalline complex (Figure 1a) consists of a broad line (g_0 = 2.10, A_0 = 65.10^4 cm^{-1}). At 111K, in MeOH/CH_2Cl_2 solution (V/V : 1/4) (Figure 1c), the complex shows a typical axial spectrum with two g values $g_{//}$ = 2.24 and $g_{\perp}$ = 2.04 indicative of a $d_{x^2-y^2}$ ground state. A hyperfine pattern is clearly visible with $A_{//}$ = 182.10^4 cm^{-1}. Theoretical and experimental studies have demonstrated that ESR parameters are quite sensitive to geometrical distortions between the planar and the tetrahedral limiting geometries in four-coordinated copper complexes.[22-25] The tendency for $g_{//}$ to increase and $A_{//}$ to decrease when the degree of tetrahedral distortion increases have been fully substantiated in the case of structurally well-characterized complexes of

TABLE VIII
Selected interatomic distances (Å) in bis (*N*-benzylpyridoxaldiminato) Cu(II)

Cu–O(1)	1.900(3)[a]	Cu–O(2)	1.900(3)
Cu–N(1)	1.967(3)	Cu–N(2)	1.964(3)
O(1)–C(1)	1.308(4)	O(2)–C(12)	1.310(4)
C(1)–C(2)	1.402(5)	C(12)–C(11)	1.405(5)
C(2)–C(3)	1.445(5)	C(11)–C(10)	1.435(5)
C(3)–N(1)	1.279(4)	C(10)–N(2)	1.286(4)
C(2)–C(4)	1.423(5)	C(11)–C(13)	1.416(5)
C(4)–C(5)	1.362(5)	C(13)–C(14)	1.359(6)
C(5)–N(3)	1.357(5)	C(14)–N(4)	1.345(5)
N(3)–C(6)	1.317(5)	N(4)–C(15)	1.329(5)
C(6)–C(1)	1.433(5)	C(15)–C(12)	1.428(5)
C(6)–C(7)	1.502(5)	C(15)–C(16)	1.494(6)
C(4)–C(8)	1.511(5)	C(13)–C(17)	1.511(5)
C(8)–O(3)	1.409(5)	C(17)–O(4)	1.411(5)
N(1)–C(9)	1.482(5)	N(2)–C(18)	1.481(5)

[a] Here and in subsequent tables. the number in parentheses is the standard deviation as obtained from the inverse matrix.

copper(II) with *N*-alkylsalicylaldiminates[24] (N_2O_2 chelate node) ($0 < \theta < 60°$. $2.23 < g_\parallel < 2.27$. $180 < A_\parallel < 145\ 10^{-4}\ cm^{-1}$. in solution in toluene) thus the g and A values observed in this work strongly suggest the occurence of relatively important distortion in their structure. The ESR spectrum of the crystallised complex b). in solution. at 293 K. shows the usual four hyperfine splitting lines characteristic of copper(II) (I = 3/2). with a $g_\parallel$ value (2.11) comparable to the calculated $\langle g \rangle$ value (2.11) obtained from c). It may be emphasized that this spectrum does not exhibit any broad structureless line which can coexist with the usual four component signal when the dihedral angle θ becomes great (>60°) as it has been assumed by Zaletov.[26]

A particular feature is observed when a solution made up of an excess of the *N*-benzylpyridoxaldimine ligand with respect to copper(II) chloride (0.1/0.01 mmoles) is studied at 92K. The spectrum may be considered as the superposition of two typical axially symetric spectra (d) with the following parameters.

$g_{\parallel 1} = 2.26$. $A_{\parallel 1} = 183$. $g = 2.06$ (form I)
$g_{\parallel 2} = 2.32$. $A_{\parallel 2} = 173$. $g = 2.06$ (form II)

These data suggest that a configurational equilibrium would occur under these conditions. This equilibrium would involve two complex species characterized by very different degree of distorsion.

X-ray Structure

The crystal structure consists of the packing of four molecules shown in Figure 2. Figure 3. which depicts the geometry of the present complex. includes the labelling scheme used elsewhere. Bond distances and bond angles are presented in Table VIII and IX. A stereoscopic view of the molecule is presented in Figure 4.

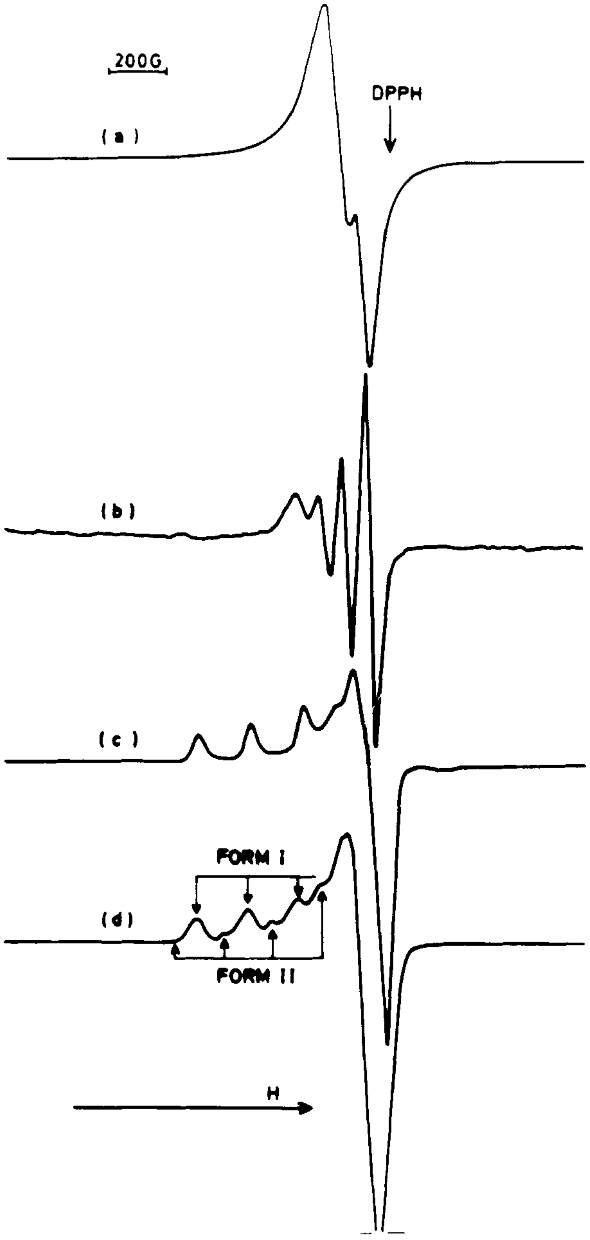

FIGURE 1 Some characteristic ESR spectra of the complex. (see Table VII for experimental conditions).

The copper atom is four coordinated to two phenolic oxygen atoms (O(1) and O(2)) and to two nitrogen atoms (N(1) and N(2)). The values of the different

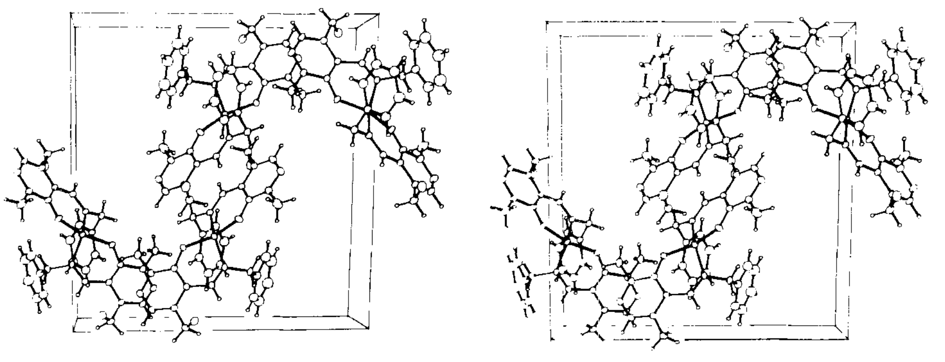

FIGURE 2 Stereoscopic view of a unit cell of the copper(II) complex. The *y* axis is horizontal from left to right, the *z* axis is vertical from bottom to top and the *x* axis comes out of the paper. The vibrational ellipsoids are drawn at the 30% level for all atoms but hydrogens which are at an arbitrary level.

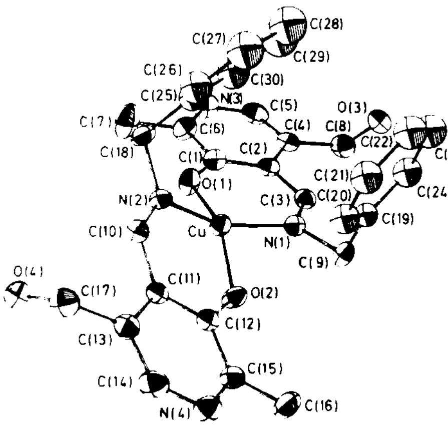

FIGURE 3 A perspective representation of the molecule of the copper(II) complex. Hydrogen atoms have been omitted for clarity. The vibrational ellipsoids are drawn at 50% probability level. The labeling scheme is also shown.

dihedral angles (see Table X) are intermediate between those of an ideal tetrahedron and those observed within an ideal square planar environment. Although the complex could be regarded as displaying a flattened tetrahedral stereochemistry, the angles at the copper atom of 91.9, 92.8, 92.7, 93.6, 154.5 and 154.9° suggest that a distortion from planarity is a more reasonable view. This distortion can be defined, according to Holm,[28] by the value of the dihedral angle θ between the two chelating moieties; in the present compound this value is 35.31°. Such a distortion has already been observed in several others (Cu(II) complexes[29] and has been mainly attributed to electronic effects. Indeed, it has been postulated on ligand-field grounds that increased electron-density on the chelate ring (especially at N) increases the tendency towards a tetrahedral configuration around Cu.

TABLE IX
Selected bond angles (deg.) in bis(*N*-benzylpyridoxaldiminato) Cu(II).

O(1)–Cu–O(2)	154.5(1)	N(2)–Cu–N(1)	154.9(1)
O(1)–Cu–N(1)	91.9(1)	O(2)–Cu–N(2)	92.8(1)
N(1)–Cu–O(2)	92.7(1)	N(2)–Cu–O(1)	93.6(1)
Cu–O(1)–C(1)	128.7(2)	Cu–O(2)–C(12)	128.4(2)
C(3)–N(1)–C(9)	116.5(3)	C(10)–N(2)–C(18)	116.6(3)
Cu–N(1)–C(3)	125.9(3)	Cu–N(2)–C(10)	124.7(3)
C(5)–N(3)–C(6)	118.1(3)	C(14)–N(4)–C(15)	118.5(4)
O(1)–C(1)–C(2)	124.8(3)	O(2)–C(12)–C(11)	124.4(3)
O(1)–C(1)–C(6)	117.4(3)	O(2)–C(12)–C(15)	117.8(3)
C(2)–C(1)–C(6)	117.9(3)	C(11)–C(12)–C(15)	117.8(3)
C(1)–C(2)–C(4)	118.6(3)	C(10)–C(11)–C(12)	122.4(3)
C(1)–C(2)–C(3)	121.6(3)	C(10)–C(11)–C(13)	119.1(3)
C(3)–C(2)–C(4)	119.4(3)	C(12)–C(11)–C(13)	118.5(3)
N(1)–C(3)–C(2)	126.0(3)	N(2)–C(10)–C(11)	127.0(3)
C(2)–C(4)–C(5)	117.8(3)	C(11)–C(13)–C(17)	122.2(3)
C(2)–C(4)–C(8)	122.5(3)	C(11)–C(13)–C(14)	118.5(4)
C(5)–C(4)–C(8)	119.6(3)	C(14)–C(13)–C(17)	119.2(3)
N(3)–C(5)–C(4)	124.6(3)	N(4)–C(14)–C(13)	124.3(3)
N(3)–C(6)–C(1)	122.6(3)	N(4)–C(15)–C(12)	122.3(4)
C(1)–C(6)–C(7)	119.1(3)	C(12)–C(15)–C(16)	120.1(4)

TABLE X
Dihedral angles (deg) for bis(*N*-benzylpyridoxaldiminato)-copper(II).

Cu, N(1), N(2)/Cu, N(2), O(2)	35.31
	δ angles[27]
O(1), O(2), N(1)/O(1), O(2), N(2)	132.42
O(1), O(2), N(1)/N(1), N(2), O(1)	146.35
O(1), O(2), N(1)/N(1), N(2), O(2)	33.87
O(1), O(2), N(2)/N(1), N(2), O(1)	33.68
O(1), O(2), N(2)/N(1), N(2), O(2)	146.57
N(1), N(2), O(1)/N(1), N(2), O(2)	130.93

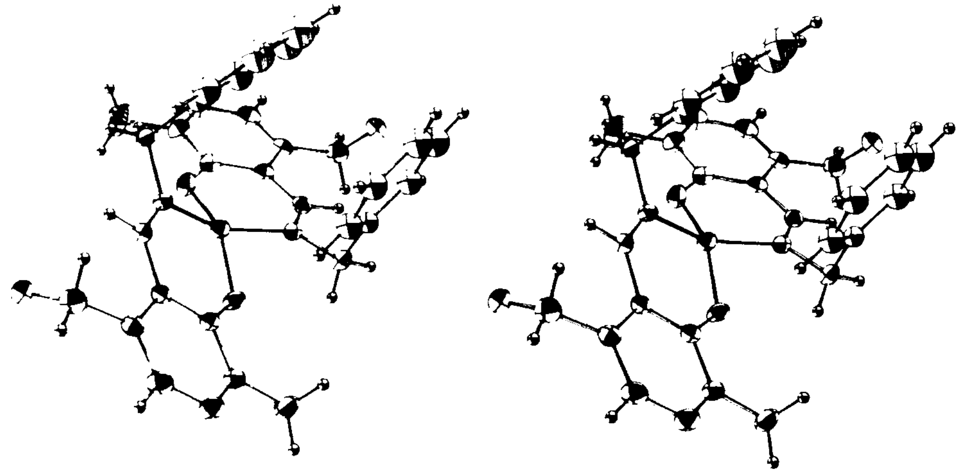

FIGURE 4 A stereoscopic view of the molecule of the copper(II) complex. The vibrational ellipsoids are drawn at 50% probability level for all atoms but H ones which are at an arbitrary level.

TABLE XI
Intermolecular contacts leading to H bonds involving four atoms of a given asymmetric unit.

O(3)–N(3)[a]	2.889 Å
O(4)–N(4)[b]	2.832 Å
N(3)–O(3)[c]	2.889 Å
N(4)–O(4)[d]	2.832 Å

[a] atom in equivalent position $\frac{1}{2} + x, \frac{1}{2} - y, z$
[b] atom in equivalent position $-\frac{1}{2} + x, -\frac{1}{2} - y, z$
[c] atom in equivalent position $-\frac{1}{2} + x, -\frac{1}{2} - y, z$
[d] atom in equivalent position $\frac{1}{2} + x, \frac{1}{2} - y, z$

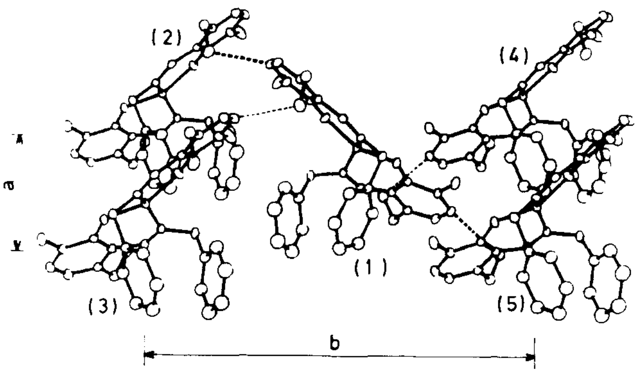

FIGURE 5 A perspective view of a running-knot showing H bonds (dashed lines). Atoms of molecules (1) to (5) belong, respectively, to the conventional 55501, 54503, 44503, 55503 and 45503 positions in which 01 and 03 are the $x\ y\ z$ and $1/2 + x$, $1/2 - y$, z equivalent positions.

Analysis of interatomic distances within an asymmetric unit shows that intramolecular approaches seem unable to account the observed distortion contradictorily with such an assumption in bis(*N*-2 phenylethyl-O-hydroxyacetophenoneimine) copper(II) complex.[30] About intermolecular interactions, four short O–N (O(4)–N(4) and O(3)–N(3)) distances varying from 2.83 to 2.84 Å (see Table XI), from a given molecule to four other neighbouring ones, are consistent with hydrogen bonds of the type OH····N. Infinite chains are thus build on these bonds; Figure 5 shows one running-knot of such a chain. We conclude that the distortion about the copper atom from planarity may be due to both electronic effect as discussed above and intermolecular interactions via rather strong OH····N type hydrogen bonds.

Figures 3, 4 and 5 show a final noticeable aspect of the molecular conformation, namely, the almost parallel phenyl groups within a given molecule. As suggested by one of the referees we checked that this feature is not responsible of the overall observed conformation of the molecule; indeed the intraplanar distance of 4.13 Å is too high to indicate attractive forces.

In conclusion, it may be emphasized that the X-ray structural determination definitively confirms the conclusions suggested by the spectroscopic data and is particularly interesting that ESR results permitted to foresee a distortion from a square planar geometry around the Cu^{2+} ion.

A sample in which a large excess of ligand with respect to Cu^{2+} (0.1/0.01 mole) is present behaves differently : two types of ESR signals are observed at low temperature. The first set (Form I) is almost identical to those related to micro-crystalline sample of the pure complex and, therefore, is attributable to this species. The second set (Form II) would belong to a second species which, taking into account the observed g and A values, should present a more distorted geometry. Hydrogen bonding may be responsible of the stability of the first species in the solid state.

As a final, remark we wish to emphasize the difference in the coordination spheres of the metal complexes of pyridoxal Schiff bases derived either from amino-acids[6–8] or from amines.[9–11] In the first case, the structural analysis reveal a square pyramidal environment of the metal, three sites being occupied by the tridentate Schiff base and the two others by solvent molecule and by donor atoms (N or O) belonging to neighbouring molecules. In the second case, two bidentate Schiff base molecules are involved in the coordination sphere leading to bis-chelate structure. The stability of such an edifice may explain the low reactivity of amines[4] in biomimetic reactions with respect to the behaviour of amino-acids.

Supplementary Material Available: lists of Fo/vs.Fc (Table V).

REFERENCES

1. E. V. Goryachenkova and E. A. Ershova in *Chemical and Biological Aspects of Pyridoxal Catalysis* (E. E. Snell, P. M. Fasella, A. Braunstein and A. Rossi Fanelli, eds), Pergamon Press, Oxford, 1963, pp. 447–452.
2. A Finazzi Agró, P. Guerrieri, M. T. Costa and B. Mondov I, *Eur. J. Biochem.*, **74**, 435–440 (1977).
3. Monoamine Oxydase and its Inhibition (Ciba Foundation Symposium 39, 1976).
4. G. A. Hamilton, *Pyridoxal Catalysis; Enzymes and Model Systems* (E. E. Snell, A. E. Braunstein, E. S. Severin and Yu M. Torchinsky, eds.), Interscience, New York, 1968, p. 375.
5. A. E. Martell, *Metal ions in biological systems* (H. Sigel, ed.), Dekker, New York, vol 2, 1973, pp. 207–268.
6. J. T. Cutfield, D. Hall and T. N. Waters, *Chem. Comm.*, 785–786 (1967).
7. G. A. Bentley, J. M. Waters and T. N. Waters, *Chem. Comm.*, 988–989 (1968).
8. K. Aoki and H. Yamazaki, *J.C.S. Chem. Comm.*, 363–365 (1980).
9. S. Yamada, Y. Kuge, I. Yamayoshi, *Inorg. Chim. Acta*, **8**, 29–32 (1974).
10. E. R. Purdy, Ph.D. Thesis, State University of New York, Stony Brook, 1976.
11. F. Nepveu, J. P. Laurent and M. Massol, *C.R. Acad. Sci. Paris*, **290**, 117–120 (1980).
12. All calculations have been performed by using the CII IRIS 80 computer of the "Centre Interuniversitaire de Calcul de Toulouse". In addition to various local programs, modified versions of the following ones were employed : Ibers' NUCLS full-matrix least-squares program, which in its non group resembles the Busing and Levy's ORFLS program; Zalkin's FOR DAP Fourier summation program : Johnson's ORTEP thermal ellipsoid plotting program : HYDRA which idealizes H atoms through a least-squares calculation (C—H = 1.00 Å).
13. A Mosset, J. J. Bonnet, J. Galy, *Acta Crystallogr. Sect B*, **33**, 2639–2644 (1977).
14. D. T. Cromer, J. T. Waber, *International Tables for X-ray cristallography*, Kyroch Press, Birmingham, England, Vol IV, 1974, Table 2.2.A. D. T. Cromer, Ibid, Table 2.3.1.
15. R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.*, **42**, 3175–3179 (1965).
16. J. A. Ibers, W. C. Hamilton, *Acta Crystallogr.*, **17**, 781–782 (1964).
17. See paragraph at end of paper regarding supplementary material.
18. B. N. Figgis and J. Lewis, *Modern Coordination Chemistry* (J. Lewis and R. G. Wilkins, ed.), Interscience, New York, London, 1980) p. 406.
19. G. C. Percy and T. A. Thornton, *J. Inorg. Nucl. Chem.*, *34*, 3357–3367 (1972).
20. K. Nakamoto, *Infrared Spectra of inorganic and coordination compounds* (J. Wiley and Sons, New York, 1963).
21. L. Sacconi and M. Ciampolini, *J. Chem. Soc.* 276 (1964).
22. Y. Murakami, Y. Matsuda and K. Sakata, *Inorg. Chem.*, **10**, 1734–1738 (1971).
23. I. Bertini, G. Canti, R. Grassi, A. Scozzafava, *Inorg. Chem.*, **19**, 2198–2200 (1980).
24. H. Yokoi, *Bull. Chem. Soc. Jpn.*, **47**, 3037–3040 (1974).
25. H. Yokoi and A. W. Addison, *Inorg. Chem.*, **16**, 1341–1349 (1977).
26. V. G. Zaletov, O. A. Osipov and V. P. Kurbatov, *Koordinats. Khim.*, **4**, 170–181 (1978).
27. E. L. Muetterties, L. J. Guggenberger, *J. Amer. Chem. Soc.*, **96**, 1748–1756 (1974).
28. R. H. Holm, M. J. O'Connor, *Progr. Inorg. Chem.*, **14**, 253 (1971).
29. H. S. Maslen, T. N. Waters, *Coord. Chem. Rev.*, **17**, 137–176 (1975) and references cited in.
30. R. M. Acheson, *An introduction to the chemistry of heterocyclic compounds*, (2nd edn., Interscience, London, 1967).