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Some Observations on the Structures of Pyridoxal-Aminoacid Schiff Base Complexes

HELEN M. DAWES, JOYCE M. WATERS and T. NEIL WATERS

Chemistry Department, University of Auckland, New Zealand

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Structures are reported for (pyridoxylidene-DL-valinato)copper(II), a = 25.640(2), c = 13.326(2) Å, γ = 120°, space group R$\bar{3}$, Z = 8 and (3-methoxysalicylidene-DL-valinato)copper(II), a = 23.515(8), b = 9.194(4), c = 17.034(6) Å, β = 126.41(7)°, space group C2/c, Z = 8. The former compound is polymeric with square-pyramidal co-ordination to copper involving five donor atoms of the ligand; the latter is monomeric with planar co-ordination geometry which includes a donor oxygen from water. Attention is drawn to bond length changes in the pyridoxylidene compound which, it is suggested, can be associated with reactivity.

Introduction

The reaction mechanisms of pyridoxal phosphate co-enzymes have been the subject of intensive investigations [1, 2] and are now well-documented as occurring through a Schiff base intermediate formed between the vitamin and the amine-containing substrate (normally an amino acid). It is also established that a metal is sometimes an additional co-factor in enzymatic catalysis by pyridoxal [3, 4] and that metals generally enhance the rate of some reactions even in the absence of enzyme [5–8]. In this instance it has been proposed that the intermediate involves a coordination complex between the metal and the Schiff base and spectrophotometric studies [7–9] as well as the isolation of solids has confirmed this suggestion [10–13].

The substituents of pyridoxal found to be essential for catalysis in non-enzymatic situations are the formyl group, the unsubstituted phenolic group in specified positions and the heterocyclic nitrogen [14, 15]. The hydroxymethyl (always present as phosphate) and methyl groups are not required for non-enzymatic reactions but are essential in biological situations. A general theory on the mechanism of these non-enzymatic reactions involves four stages [14–16]:

(1) Formation of a Schiff base with subsequent electron displacement from the α-carbon atom to the electronegative ring nitrogen through a conjugated system of double bonds. Weakening of the bonds to the α-carbon thus results.

(2) Release of H^+, $COOH^+$ or R^+ from the α-carbon to produce a transitional Schiff base.

(3) Localization of the lone pair of electrons of the heterocyclic nitrogen either onto the α-carbon for racemization and decarboxylation or onto the formyl carbon for transamination. Protonation at the α-carbon then occurs for all reactions except that involving initial labilization of a α-hydrogen. In this instance subsequent protonation can occur either at the α-carbon or at the formyl carbon (transamination).

(4) Hydrolysis of the carbon–nitrogen bond to give the products.

Pullman *et al.* [17] have since attempted a further investigation by calculating the energy changes associated with postulated transitional states of the Schiff base and conclude that the fundamental factors are variations in resonance energy and electronic distribution among the possible states. They further conclude that inductive effects leading to bond weakening at the α-carbon of the amino acid cannot be a major driving force. On the other hand it is noted that when valine or isoleucine are reactants non-enzymatic transamination is very slow [5], despite the high stability of their Schiff bases, suggesting that in these two instances energy changes involve the amino acid and are not, as might be implied from the above, confined to the conjugated pyridoximine portion. In this connection claims that changes in bond geometries and electronic distributions can be detected in coordination complexes assume some interest [18].

Evidence for such changes in the ground state was therefore sought from the X-ray determination of the structures of two compounds. One, the Schiff base intermediate of pyridoxal and valine, with copper as coordinating centre, involves the biological cofactor whereas the other was chosen to be similar but used a substituted salicylaldehyde rather than a hydroxypyridine aldehyde. It was not only hoped to make a comparison between the two but also to seek evidence for the participation of the amino acid substituents in the overall electronic redistribution.

A number of earlier X-ray investigations have been made on pyridoxal intermediates [19, 22] but none have achieved the level of accuracy which would make electronic changes manifest. Indeed, difficulty has often been encountered in obtaining good crystals and of maintaining them during X-ray data collection [19]. The analysis involving pyridoxal (compound I) was, therefore, a reinvestigation of a compound previously studied [20] in an attempt to improve the reliability of structural information. The second compound (II) was prepared for the present study.

Experimental

Preparation

Compound I (pyridoxylidene-DL-valinato)copper(II) was prepared as previously described [10], crystallisation occurring overnight at 5 °C on addition of an equal volume of ethanol to the methanol/water reaction mixture. Many combinations of solvents were tried in attempting recrystallisation. Decomposition invariably occurred and crystal had to be grown from the reaction solution. An approximately rectangular dark-green crystal, 0.27 × 0.22 × 0.17 mm in dimensions, was used for data collection on a Hilger–Watts Y290 instrument.

Preparation of compound II (3-methoxysalicylidene-DL-valinato)copper(II) was accomplished by standard methods involving the preparation of the Schiff base followed by reaction with cupric acetate monohydrate in an ethanol/water mixture. Again recrystallisation proved difficult, the complex being relatively insoluble, and seeding of slowly evaporating mother liquor gave the best results. A crystal, 0.30 × 0.15 × 0.30 mm, was used for data collection.

Crystal Data

I: $C_{13}H_{14}CuN_2O_4$, $M = 325.8$. Trigonal, $a = 25.640(2)$, $c = 13.326(2)$ Å, $\gamma = 120°$ (standard deviations from the least squares setting of 12 diffractometer setting angles), $U = 7587$ Å^3, $Z = 18$, $F(000) = 5864$. Cu-K$_\alpha$ radiation, $\lambda = 1.5418$ Å, $\mu = 19.8$ cm^{-1}. Space group $R\bar{3}$.

Data were collected by the $\omega/2\theta$ technique with a 2θ scan of 1.60° stepped at a rate of 0.01° sec^{-1}. A total of 2,623 reflexions were measured of which 1,063 had an intensity greater than $3\sigma(I)$. Absorption corrections were not made. Although a structure analysis had been earlier completed the choice of a reversed coordinate system in that instance and the occurrence of some apparent anomalies in the conversion of coordinates persuaded us to proceed through standard heavy-atom procedures. The same overall structure was recovered. At the appropriate stage a difference map revealed all hydrogen atoms (which were then included in the model at standard geometries) except that expected on O(1). No hydrogen was seen on N(1), the heterocyclic nitrogen. Conversion to anisotropic temperature parameters brought the R factor to 0.129. There then followed a period of inconclusive refinement while attempts were made to account for the water molecules. Difference maps showed two maxima large enough to be water and three smaller peaks (electron density approximately 0.9 e Å^{-3}) in a region subsequently seen to represent channels running through the structure in the c direction. Various stratagems to fix occupancy values and temperature factors were used but none were satisfactory and the lowest R-factor (0.080) was obtained with only the two molecules included. The other maxima remained and possibly represent positions of traces of water which continued to leave the crystal during data collection. The two molecules are in stereochemically acceptable positions, one being hydrogen bound to O(3), the other being linked to it so that they form, together, a chain running through the channels in the structure.

Final atom coordinates are listed in Table I and bond lengths and angles in Tables II and III. Structure factor and temperature parameter data are deposited. The numbering system is that of Fig. 1.

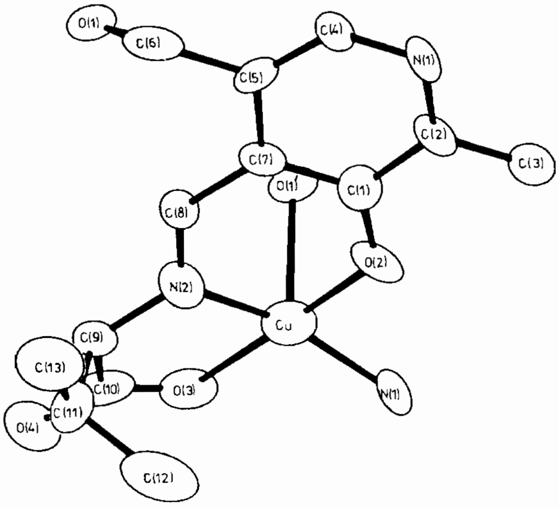

Fig. 1. Diagram of the molecular unit of I.

The molecule is centred on five-coordinate copper in square-pyramidal stereochemistry. The phenolic oxygen, imine nitrogen and carboxyl oxygen atoms of the tridentate Schiff base occupy three corners of the coordination square, the remaining in-plane position being filled by the heterocyclic nitrogen of a neighbouring molecule. Binding by the hydroxymethyl oxygen of yet another moiety in the fifth apical site completes the square-pyramid. The resulting polymeric structure is further stabilised by hydrogen bonding through a solvent molecule (O(3)–O(5) = 2.98(3) Å). Both waters of hydration occupy

TABLE I. Atom Co-ordinates of I.

Atom	x/a	y/b	z/c
Cu	0.5677(1)	0.0386(1)	0.2686(2)
O(1)	0.4041(5)	−0.0918(6)	0.5806(8)
O(2)	0.5935(5)	0.0122(5)	0.3259(9)
O(3)	0.5318(7)	0.0830(6)	0.2060(9)
O(4)	0.4442(7)	0.0789(6)	0.1711(10)
N(1)	0.5781(7)	−0.1084(7)	0.5302(12)
N(2)	0.4845(7)	−0.0158(8)	0.3071(11)
C(1)	0.5682(10)	−0.0493(9)	0.4016(15)
C(2)	0.6013(8)	−0.0699(8)	0.4529(14)
C(3)	0.6624(8)	−0.0521(8)	0.4212(13)
C(4)	0.5212(11)	−0.1273(10)	0.5606(13)
C(5)	0 4854(9)	−0.1101(9)	0.5185(13)
C(6)	0.4177(9)	−0.1361(10)	0.5522(14)
C(7)	0.5067(10)	−0.0687(8)	0.4336(13)
C(8)	0.4668(9)	−0.0548(9)	0.3840(13)
C(9)	0.4408(9)	−0.0059(10)	0.2540(12)
C(10)	0.4726(13)	0.0574(10)	0.2068(15)
C(11)	0.4058(9)	−0.0536(10)	0.1770(15)
C(12)	0.3648(11)	−0.1174(12)	0.2189(17)
C(13)	0.4505(11)	−0.0576(11)	0.1021(15)
H(31)	0.659	−0.068	0.348
H(32)	0.687	−0.007	0.421
H(33)	0.688	−0.068	0.457
H(4)	0.504	−0.157	0.625
H(61)	0.391	−0.162	0.493
H(62)	0.410	−0.167	0.610
H(8)	0.420	−0.050	0.400
H(9)	0.407	−0.008	0.305
H(11)	0.380	−0.041	0.134
H(121)	0.368	−0.118	0.293
H(122)	0.321	−0.133	0.198
H(123)	0.393	−0.123	0.170
H(131)	0.476	−0.073	0.141
H(132)	0.428	−0.088	0.045
H(133)	0.478	−0.017	0.074
O(5)	0.5979(11)	0.2105(12)	0.1432(28)
O(6)	0.5731(19)	0.2969(17)	−0.0006(31)

TABLE II. Bond Lengths in I (Å).

Cu–O(2)	1.90(1)
Cu–O(3)	1.97(1)
Cu–O(1)′	2.33(1)
Cu–N(2)	1.95(1)
Cu–N(1)′	2.02(1)
O(1)–C(6)	1.40(2)
O(2)–C(1)	1.32(2)
O(3)–C(10)	1.32(2)
O(4)–C(10)	1.21(2)
N(1)–C(2)	1.34(2)
N(1)–C(4)	1.36(2)
N(2)–C(8)	1.34(2)
N(2)–C(9)	1.46(2)
C(1)–C(2)	1.39(2)
C(1)–C(7)	1.45(3)
C(2)–C(3)	1.45(2)
C(4)–C(5)	1.32(2)
C(5)–C(6)	1.59(2)
C(5)–C(7)	1.46(2)
C(7)–C(8)	1.40(2)
C(9)–C(10)	1.54(3)
C(10)–C(11)	1.50(2)
C(11)–C(12)	1.54(3)
C(11)–C(13)	1.56(3)

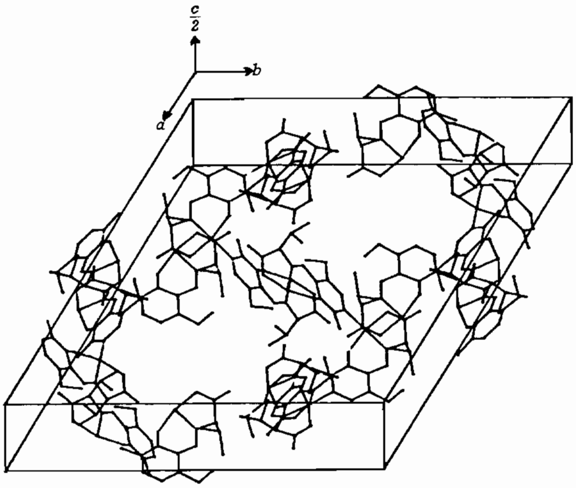

Fig. 2. Packing diagram of I illustrating the channels parallel to *c*.

channels running through the crystal parallel to the *c*-axis (Fig. 2) and are also hydrogen bonded together (O(5)–O(6) = 2.95(5) Å).

The heterocyclic ring is planar, the largest deviation from the plane of best fit being 0.009 Å by C(1). The chelate rings are much less planar, the six-membered ring being characterised by a bend across the line N(2)....O(2), to give the 'step' conformation often seen in ligands coordinated to copper(II). The need to close the rings and the presence of tetrahedrally bonded C(9) ensures this lack of planarity. The coordination geometry about the metal also differs from ideal in that the four in-plane donors show a small, but significant, (0.05–0.09 Å) tetrahedral deviation. Pertinent data are listed in Table IV.

The heterocyclic nitrogen is not protonated in contrast with the other pyridoxylidene complexes which have been investigated. Instead it is bound to copper and, presumably as a consequence, its internal bond angle, C(2)–N(1)–C(4), of 120.4° is between the mean non-protonated (115.7°) and protonated (125.0°) values [23].

Crystal Data

II: $C_{13}H_{15}CuNO_4$, M = 298.8. Monoclinic, a = 23.515(8), b = 9.194(4), c = 17.034(6) Å, β = 126.41(3)° (standard deviations from 12 diffractometer setting angles), U = 2963 Å^3, Z = 8, $F(000)$ = 2390, Mo-K$_\alpha$ radiation, λ = 0.7107 Å, μ = 15.4 cm^{-1}. Space group $C_{2/c}$.

TABLE III. Bond Angles in I (degrees).

O(2)–Cu–N(1)′	92.0(9)
O(2)–Cu–N(2)	91.9(8)
O(3)–Cu–N(1)′	92.8(9)
O(3)–Cu–N(2)	82.6(8)
O(1)′–Cu–O(2)	86.6(8)
O(1)′–Cu–O(3)	97.2(8)
O(1)′–Cu–N(1)′	97.0(8)
O(1)′–Cu–N(2)	95.9(7)
Cu–O(2)–C(1)	126(1)
Cu–O(3)–C(10)	118(1)
C(2)–N(1)–C(4)	120(2)
Cu–N(2)–C(8)	125(1)
Cu–N(2)–C(9)	114(2)
C(8)–N(2)–C(9)	120(1)
O(2)–C(1)–C(2)	117(2)
O(2)–C(1)–C(7)	123(1)
C(2)–C(1)–C(7)	120(1)
N(1)–C(2)–C(1)	121(2)
N(1)–C(2)–C(3)	118(2)
C(1)–C(2)–C(3)	121(2)
N(1)–C(4)–C(5)	123(1)
C(4)–C(5)–C(6)	123(2)
C(4)–C(5)–C(7)	120(1)
C(6)–C(5)–C(7)	117(1)
O(1)–C(6)–C(5)	114(1)
C(5)–C(7)–C(1)	115(2)
C(8)–C(7)–C(1)	125(1)
C(5)–C(7)–C(8)	120(1)
N(2)–C(8)–C(7)	122(1)
N(2)–C(9)–C(10)	110(1)
N(2)–C(9)–C(11)	113(1)
C(10)–C(9)–C(11)	112(2)
O(3)–C(10)–O(4)	125(1)
O(3)–C(10)–C(9)	114(1)
O(4)–C(10)–C(9)	121(1)
C(9)–C(11)–C(12)	116(1)
C(9)–C(11)–C(13)	109(1)
C(12)–C(11)–C(13)	107(2)

Data were collected by Dr F. van Meurs, Enraf-Nonius Company, Delft, on a Nonius CAD4 automatic diffractometer using the $\omega/2\theta$ technique. A total of 5277 reflections were measured, 1646 having an intensity greater than $3\sigma(I)$. Absorption corrections were not applied.

Statistical tests favoured the centrosymmetric space group and an analysis of the Patterson map gave the positions of the copper atoms. A y-coordinate of 0.25 and 0.75 made application of the heavy atom method more difficult than expected but repeated use of electron density maps eventually revealed the molecule and led to the detection of hydrogen atoms. After refinement using anisotropic thermal parameters a final difference map confirmed that all electron density had been accounted for. The R factor was 0.054. Atom coordinates are listed in Table V and structure factor and thermal parameter data are deposited. Bond lengths and angles are in Tables VI and VII. The numbering system is, as far as possible, that used for compound I. It is shown in Fig. 3.

Structure II. The molecule is again a 1:1 complex but this time the metal is four-coordinate with planar geometry, one donor position being filled by a water molecule. A further water molecule has a hydrogen bonding function. The benzene ring is

TABLE IV. Planes of Best Fit, Compound I.

Atom	Plane 1	Plane 4	Atom	Plane 1	Plane 4
N(1)	0.00(2)*		N(2)	0.06(2)	0.09(2)*
C(1)	0.01(2)*	−0.40(2)	Cu	−0.474(3)	−0.125(3)
C(2)	−0.01(2)*		O(2)	0.00(1)	−0.05(1)*
C(4)	0.01(2)*		O(1)′	−2.65(1)	−2.44(1)
C(5)	−0.00(2)*		N(1)′	−0.65(2)	0.08(2)*
C(7)	−0.00(2)*	−0.56(2)	O(3)	−0.80(1)	−0.07(1)*
C(3)	0.02(2)		C(10)	−0.43(2)	0.20(2)
C(6)	0.09(2)		O(4)	−0.56(1)	
O(1)	−0.96(1)		C(9)	0.27(2)	0.50(2)
C(8)	0.10(2)	−0.25(2)	C(11)	1.72(2)	
			C(12)	2.46(3)	
			C(13)	2.48(2)	

*Atoms forming plane.

Coefficients and χ^2 for plane $ax + by + cz + d = 0$

	a	b	c	d	χ^2
1	0.0558	−0.7784	−0.6253	−1 6460	0.4767
4	0.0390	−0.5745	−0.8176	−2.7452	113.5675

TABLE V. Atomic Coordinates, Compound II.

Atom	x/a	y/b	z/c
Cu	0.4921(1)	0.2324(1)	0.0600(1)
O(1)	0.3154(4)	−0.0864(7)	−0.0695(5)
O(2)	0.4248(3)	0.0821(6)	0.0144(4)
O(3)	0.5632(3)	0.3810(6)	0.1023(4)
O(4)	0.6786(3)	0.4195(6)	0.1994(4)
O(5)	0.4172(3)	0.3648(6)	−0.0337(4)
O(6)	0.3148(3)	0.1804(7)	−0.1652(4)
N(1)	0.5693(3)	0.1196(7)	0.1631(4)
C(1)	0.4367(5)	−0.0510(9)	0.0477(6)
C(2)	0.3781(5)	−0.1470(10)	0.0047(6)
C(3)	0.2521(5)	−0.1660(10)	−0.1121(7)
C(4)	0.3859(5)	−0.2900(10)	0.0364(6)
C(5)	0.4528(6)	−0.3420(10)	0.1107(7)
C(6)	0.5113(5)	−0.2570(10)	0.1527(6)
C(7)	0.5041(4)	−0.1065(9)	0.1231(6)
C(8)	0.5675(5)	−0.0186(9)	0.1737(6)
C(9)	0.6369(4)	0.1972(8)	0.2214(5)
C(10)	0.6276(4)	0.3441(9)	0.1718(5)
C(11)	0.6631(4)	0.2290(10)	0.3279(6)
C(12)	0.6919(6)	0.0890(10)	0.3928(7)
C(13)	0.6063(5)	0.3080(10)	0.3307(7)
H(3)A	0.2566	−0.2651	−0.1314
H(3)B	0.2466	−0.1818	−0.0548
H(3)C	0.2043	−0.1236	−0.1655
H(4)	0.3437	−0.3559	0.0142
H(5)	0.4569	−0.4493	0.1293
H(6)	0.5604	−0.3005	0.2029
H(8)	0.6153	−0.0694	0.2283
H(9)	0.6771	0.1359	0.2281
H(11)	0.7046	0.3003	0.3513
H(12)A	0.6831	−0.0048	0.3559
H(12)B	0.7463	0.0945	0.4481
H(12)C	0.6562	0.1378	0.3987
H(13)A	0.6234	0.4112	0.3590
H(13)B	0.5602	0.3119	0.2669
H(13)C	0.6262	0.2176	0.3754

TABLE VI. Bond Lengths in II (Å).

Cu–O(2)	1.885(5)
Cu–O(3)	1.934(5)
Cu–O(5)	1.957(5)
Cu–N(1)	1.927(6)
O(1)–C(2)	1.37(1)
O(1)–C(3)	1.41(1)
O(2)–C(1)	1.310(9)
O(3)–C(10)	1.302(8)
O(4)–C(10)	1.211(9)
O(5)–O(6)	2.711(7)
N(1)–C(8)	1.288(9)
N(1)–C(9)	1.465(9)
C(1)–C(2)	1.42(1)
C(1)–C(7)	1.42(1)
C(2)–C(4)	1.40(1)
C(4)–C(5)	1.40(1)
C(5)–C(6)	1.36(1)
C(6)–C(7)	1.45(1)
C(7)–C(8)	1.45(1)
C(9)–C(10)	1.55(1)
C(9)–C(11)	1.59(1)
C(11)–C(12)	1.57(1)
C(11)–C(13)	1.55(1)

planar (Table VIII). The two chelate rings are somewhat more planar than in the pyridoxal-containing complex although a tetrahedral distortion of about the same magnitude is still apparent in the arrangement of donors about the metal. The overall increase in planarity is a sign of stronger copper to ligand binding as is the absence of a fifth donor atom and a shortening of all the copper-donor bonds by 0.02 to 0.06 Å.

TABLE VII. Bond Angles in II (degrees).

O(2)–Cu–N(1)	95.08(2)	C(2)–C(4)–C(5)	119.74(6)
O(3)–Cu–N(1)	84.41(3)	C(4)–C(5)–C(6)	121.67(6)
O(2)–Cu–O(5)	89.39(2)	C(5)–C(6)–C(7)	119.55(6)
O(3)–Cu–O(5)	91.43(3)	C(6)–C(7)–C(1)	119.95(6)
C(2)–O(1)–C(3)	119.43(6)	C(8)–C(7)–C(1)	122.82(5)
Cu–O(2)–C(1)	126.39(3)	C(6)–C(7)–C(8)	117.23(5)
Cu–O(3)–C(10)	115.85(3)	N(1)–C(8)–C(7)	125.09(4)
Cu–O(5)–O(6)	102.83(1)	N(1)–C(9)–C(10)	107.78(5)
Cu–N(1)–C(8)	124.75(3)	N(1)–C(9)–C(11)	113.81(5)
Cu–N(1)–C(9)	114.57(3)	C(10)–C(9)–C(11)	108.47(5)
C(8)–N(1)–C(9)	119.79(5)	O(3)–C(10)–O(4)	123.57(6)
O(2)–C(1)–C(2)	117.60(6)	O(3)–C(10)–C(9)	116.36(5)
O(2)–C(1)–C(7)	124.75(6)	O(4)–C(10)–C(9)	120.06(5)
C(2)–C(1)–C(7)	117.65(6)	C(9)–C(11)–C(12)	112.84(5)
O(1)–C(2)–C(1)	113.91(4)	C(9)–C(11)–C(13)	112.03(5)
O(1)–C(2)–C(4)	124.72(4)	C(12)–C(11)–C(13)	112.09(6)

TABLE VIII. Planes of Best Fit, Compound II.

Atom	Plane 1	Plane 4	Atom	Plane 1	Plane 4
C(1)	−0.00(1)*	0.09(1)	N(1)	−0.209(8)	−0.089(8)*
C(2)	0.01(1)*		Cu	−0.057(1)	0.007(1)
C(4)	−0.01(1)*		O(2)	0.004(7)	0.069(7)*
C(5)	−0.01(1)*		O(3)	0.001(7)	0.065(7)*
C(6)	0.02(1)*		O(5)	−0.074(7)	−0.066(7)*
C(7)	−0.01(1)*	0.13(1)	O(6)	0.918(7)	0.909(7)
O(1)	0.062(8)		C(10)	−0.00(1)	0.10(1)
C(3)	−0.05(1)		O(4)	0.167(7)	0.10(1)
C(8)	−0.05(1)	0.09(1)	C(9)	−0.282(9)	
			C(11)	−1.69(1)	
			C(12)	−1.92(1)	
			C(13)	−2.86(1)	

*Atoms forming plane.

Coefficients and χ^2 for plane ax + by + cz + d = 0

	a	b	c	d	χ^2
1	0.6843	−0.2858	−0.6708	6.3809	5.0498
4	0.6952	−0.3041	−0.6513	6.4139	406.5145

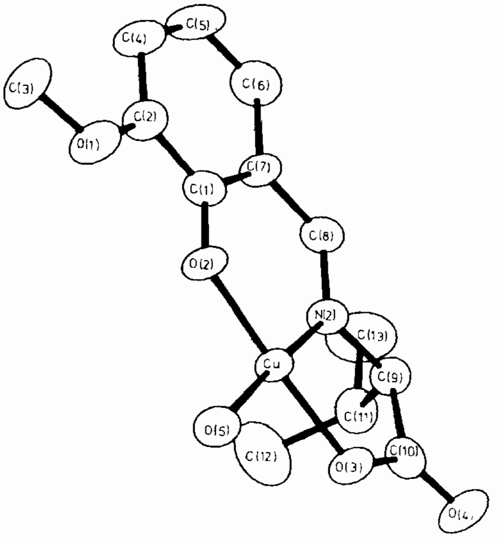

Fig. 3. Diagram of II.

Discussion

Although the final R factor of 0.080 for I is better than the value of 0.139 previously obtained with film data it is still disappointingly high. We attribute this to a variation in water content, as molecules left the crystal during data collection. The standard deviations in bond lengths and angles are still large, a criticism which applies to all published structures of pyridoxal/amino-acid metal complexes giving these data. Comparisons with appropriate complexed and uncomplexed compounds do, nevertheless, show some interesting differences to which we shall refer, believing that the sum total of changes makes a plausible hypothesis even though individual values can be disputed.

Such comparisons with the structures of the uncomplexed pyridoxime phosphate [24], pyridoxamine phosphate hydrochloride [25] and L-valine·HCl [27], which have standard deviations between 0.02 and 0.002 Å in carbon–carbon bonds, are indicated in Table IX as bond differences. Before conclusions are drawn some changes due to circumstances should be acknowledged. Thus atoms O(1) and O(2), O(3) and N(1) are coordinated in I.

The pattern of changes is not altogether the one presented by a similar compound, bis(pyridoxylidene-DL-valinato)nickel(II) [22], where, although the standard deviations (0.02 Å) are not small, a comparison of measurements between the two ligands in the asymmetric unit reveals excellent agreement. Differences between these bond lengths and those found in an uncomplexed molecule are also shown in Table IX. Comparison with bis(pyridoxylidene-DL-valinato)-manganese(II) [19] gives almost identical figures.

It seems that compound I differs from other complexes of this type and also from the N-pyridoxylidene-N′-salicyloylhydrazinato complex of copper(II) [28] in showing bond shortening at C(1)–C(2) (by about 0.02 Å), C(4)–C(5) (by 0.05 Å), C(7)–C(8) (0.04 Å) and lengthening at C(8)–N(2) (by 0.03 Å) and C(5)–C(7) (0.05 Å). It is as if the pyridoxal moiety were to some extent locked into the

TABLE IX. Differences (Å) of Bond Lengths in I from those in similar Compounds.[a]

Bond	1–2	1–3	1–4	1–5	6–2
C(1)–C(2)	–0.02	–0.02	–0.02		0.03
C(1)–O(2)	–0.03	–0.02	–0.02		–0.06
C(2)–C(3)	–0.07	–0.05	–0.06		–0.02
C(2)–N(1)	–0.01	–0.02	0.02		–0.01
N(1)–C(4)	0.02	0.01	0.02		–0.02
C(4)–C(5)	–0.04	–0.05	–0.06		0
C(5)–C(6)	0.04	0.06	0.07		–0.05
C(6)–O(1)	–0.03	0	–0.02		–0.02
C(5)–C(7)	0.05	0.05	0.05		0
C(7)–C(1)	0.07	0.04	0.05		0.05
C(7)–C(8)	–0.04		–0.06		0.02
C(8)–N(2)	0.03		0.05		–0.03
N(2)–C(9)				–0.03	
C(9)–C(10)				0.02	
C(10)–O(3)				0.12	
C(10)–O(4)				–0.10	
C(9)–C(11)				–0.04	
C(11)–C(12)				0.02	
C(11)–C(13)				0.04	

1 = Compound I
2 = Pyridoxime phosphate (Ref. 24)
3 = Pyridoxamine phosphate, HCl (Ref. 25)
4 = Pyridoxylidene aniline (Ref. 26)
5 = L-valine, HCl (Ref. 27)
6 = Bis(pyridoxylidene-DL-valinato)nickel(II) (Ref. 22)

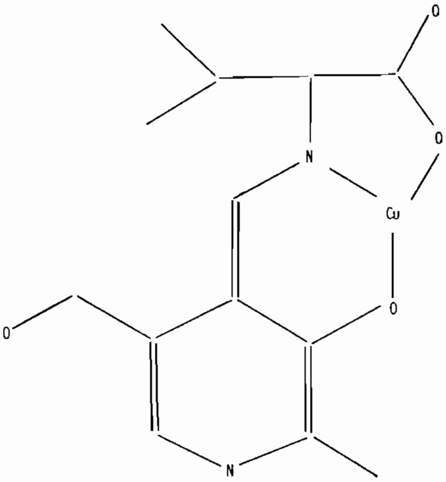

Fig. 4. A canonical representation of the observed bond shortening in I.

quinonoid form formally postulated as occurring during the reaction sequence. Unfortunately the accuracy of the results do not allow the argument to be pushed too far but it is tempting to see the lengthened C(9)–C(10) bond as further evidence for an electron redistribution. On the other hand the C(9)–C(11) bond appears to have appreciably shortened (by 0.04 Å when compared with valine•HCl) in contrast to the lengthening normally seen in pyridoxylidene complexes and in compound II (where it is 0.05 Å longer than the valine•HCl value).

We therefore conclude that an electronic redistribution is to be seen in the ground state of compound I and that this disposes it towards reactivity. The changes can be visualised in terms of canonical contributions, one of which is shown in Fig. 4 and in this connection it is interesting to note the shortening of C(2)–C(3) on Schiff base and complex formation. The enhanced manifestation of hyperconjugative effects under metal binding, postulated elsewhere [18], may even account, in some small part, for the biological requirements for the methyl group.

A recent communication reports the structures of the nickel(II) and copper(II) complexes with pyridoxal and O-phospho-DL-threonine [29]. It comments on the in-plane position of the hydrogen atom of the α-carbon of the amino-acid in connection with Dunathan's hypothesis [30] for C–H bond-breaking during catalysis. In contrast with this situation the α-hydrogen atom of I is appreciably out of the aldimine plane (by 0.7 Å). This could be read as confirming the suggestion of the bond lengths that this molecule is predisposed to reaction. However, in II, which is not expected to show catalytic activity, this hydrogen is even further from the aldimine plane (0.8 Å); it seems that chelate ring closure through the carboxylates and, in the O-phospho-DL-threonine compound mentioned above, the requirements of hydrogen bonding to the phosphate, must largely dictate the position of the α-hydrogen.

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