

## Schiff Base Complexes of Copper(II)\*

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The crystal structures of four Schiff base molecules are presented, one of which is a re-appraisal of a previously reported structure. Crystals of *N,N'*-1,2-phenylene-bis(salicylideneiminato)copper(II) have been grown from both chloroform and pyridine. The structure from chloroform shows two crystallographically distinct square-planar molecules per asymmetric unit in an orthorhombic cell,  $a = 20.159(2)$ ,  $b = 14.918(1)$ ,  $c = 13.329(1)$  Å; space group  $Pna2_1$ . Two different stereochemistries are observed when pyridine is the solvent. One has square planar geometry and the other square pyramidal with a pyridine molecule bound in the fifth co-ordination site. The space group is  $P\bar{1}$  with  $a = 8.748(4)$ ,  $b = 14.499(4)$ ,  $c = 18.725(5)$  Å,  $\alpha = 109.93(3)$ ,  $\beta = 91.99(2)$ ,  $\gamma = 101.64(3)^\circ$ . Bis(*N*-phenylpyridoxylideneiminato)copper(II) crystallises in a monoclinic cell, space group  $P2_1/c$ ,  $a = 5.7037(6)$ ,  $b = 20.394(1)$ ,  $c = 10.6321(6)$  Å,  $\beta = 101.443(6)^\circ$  with the *trans* square planar co-ordination geometry. In the re-appraised structure of aqua(5-phosphopyridoxylidene-DL-phenylalanineato)copper(II) the complex is square pyramidal with two oxygen and one nitrogen donor from the ligand. The fourth site is occupied by a water molecule and the fifth, apical donor is a phosphate oxygen from an adjacent molecule. The space group is triclinic  $P\bar{1}$  with  $a = 8.697(2)$ ,  $b = 13.039(3)$ ,  $c = 12.418(3)$  Å,  $\alpha = 110.49(2)$ ,  $\beta = 108.61(2)$ ,  $\gamma = 63.65(10)^\circ$ .

**Key words:** copper(II) complexes, Schiff base complexes, salicylideneiminato complexes, pyridoxal.

\* Dedicated to Professor Boris Kamenar on the occasion of his 70<sup>th</sup> birthday.

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## INTRODUCTION

Ligands derived from substituted salicylaldimine have played an important part in revealing the preferred co-ordination geometries of metal complexes. Of particular interest have been those involving copper(II) since they reveal surprising molecular diversity not only in co-ordination geometry but in more subtle changes in the ligands. Thus complexes with four, five or six donors or with marked tetrahedral »distortions« are accompanied by bond length changes and deviations from expected ligand geometry.<sup>1-3</sup> So-called »stepped« or »umbrella« distortions are well documented with deviations from planarity and unexpected bond lengths in the aromatic ring of salicylaldiminato (salim) groups also being claimed.<sup>4,5</sup> Of interest is the variety of geometries which are adopted by the same complex or by complexes which have minor changes in constituents or in packing arrangements. Thus bis(*N*-methylsalim)Cu(II) is perfectly planar in one crystal form,<sup>6</sup> planar but stepped in another<sup>7</sup> and square-pyramidal and dimeric in a third.<sup>8</sup> None of these crystals contains solvent or other adduct molecules. Bis(*N*-ethylsalim)Cu(II), in contrast, adopts a partially tetrahedral molecular structure in the three crystallographically independent molecules in two different crystalline forms.<sup>9-11</sup> If the R-group on the nitrogen is switched to *n*-propyl the copper complex is planar again<sup>12</sup> but the *i*-propyl derivative is partially tetrahedral.<sup>13</sup> Thus, apart from packing considerations or the intra-molecular steric interactions thought to give rise to molecular stepping,<sup>14,15</sup> there seem to be electronic influences also at work. It has been postulated that substituents which »load« or help stabilise electron density on the oxygen donors bring about molecular stepping in otherwise planar complexes. Electron density loaded onto nitrogen donors, on the other hand, induces a tetrahedral distortion at copper. Additionally it has been postulated that a decrease in the »ligand field« at the four donor atoms contributes to an increase in co-ordination number from four to five or six,<sup>5</sup> the extra donors arising from the sharing of atoms between metal centres, the incorporation of solvent molecules or even from interactions of the »charge transfer« type with adjacent aromatic rings. It has also been noticed that hydrogen bonding to the donor oxygen atoms leads to a return to four-coordinate planar stereochemistry at copper and an increased overall planarity of the complex.<sup>5</sup> More accurate re-determinations of structures, such as those undertaken by Kamenar and his co-workers,<sup>16-19</sup> help test these hypotheses more rigorously.

Although the changes to co-ordination geometry resulting from these electronic effects are readily demonstrated, more subtle molecular adjustments, such as bond length changes or small deviations from expected ligand geometry, are not so readily apparent because they are often at the

limits of quantitative determination. Instead, an accumulation of evidence has had to be used in promoting the view that electronic redistribution is an important factor in these complexes and accompanies conformational adjustments.

To this end we have determined the crystal structures of chloroform and pyridine solvates of the quadridentate molecule *N,N'*-1,2-phenylenebis(salim)Cu(II) – compounds **1** and **2** – and the structures of copper(II) complexes based on two ligands derived from the molecule 2-methyl-3-hydroxy-4-iminomethyl-5-hydroxymethylpyridine, *i.e.* pyridoximine (pyrim) a derivative of the biological co-factor pyridoxal. These were bis(*N*-phenylpyrim)Cu(II) – compound **3** – and aqua(5-phosphopyridoxylidene-DL-phenylalanineato)Cu(II) – compound **4**. A note on the structure of **4** derived from film data<sup>20</sup> had previously been published but, because of its relative inaccuracy ( $R = 0.145$ ) and difficulties with locating water molecules, a further analysis using diffractometer measurements was undertaken. Shortly after this was completed such an analysis ( $R = 0.073$ ) appeared in the literature.<sup>21</sup> Accordingly our reappraisal was laid aside. We noted, however, that there was a discrepancy in the number of water molecules located, with a correspondingly larger volume ( $32 \text{ \AA}^3$ ) in the cell we had determined. We also noted that the methods of preparation were different. Although both analyses report on the structure of a pyridoxylidene-DL-phenylalanine complex the literature account used L-phenylalanine as starting material and relied on racemisation to produce the mixture. Our further results are therefore briefly described so as to compare them with the 1991 report<sup>21</sup> and with the possibility of linking minor geometrical changes with the more extensive information available from the salim series.

## EXPERIMENTAL

### *Preparation of N,N'-1,2-Phenylene-bis(salicylideneiminato)copper(II)*

*N,N'*-1,2-Phenylene-bis(salicylideneiminato)copper(II) was prepared as previously described.<sup>22</sup> Recrystallisation was from chloroform (**1**) and pyridine (**2**). The crystals obtained from either solvent were susceptible to solvent loss and those selected for data collection had to be sealed in quartz capillaries with mother liquor.

### *Preparation of Bis(N-phenylpyridoxylideneiminato)copper(II)*

A few drops of aniline were added to an aqueous solution of pyridoxal ( $0.1 \text{ g}$  in  $10 \text{ cm}^3$ ) to give a yellow solution. To this was added  $10 \text{ cm}^3$  of a saturated copper acetate solution. Golden-brown crystals (**3**) were obtained from the green solution by vapour diffusion using ethanol as the diffusing solvent.

*Preparation of  
Aqua(5-phosphopyridoxylidene-DL-phenylalanineato)copper(II)*

A modified literature procedure<sup>20</sup> was employed with the addition of DL-phenylalanine (0.1 g) to pyridoxal-5-phosphate (0.15 g) in 10 cm<sup>3</sup> water. The resulting yellow solution was heated before adding saturated copper acetate solution until a slight cloudiness persisted. Dilute HCl was then added dropwise until this precipitate just dissolved. Green plate-like crystals were then obtained by slow vapour diffusion using ethanol as the diffusing solvent. Most were very small and very thin but eventually one marginally suitable for X-ray data collection was obtained (**4**).

*X-Ray Structural Analyses*

Three of the four data sets were collected with a Hilger-Watts Y290 diffractometer but for the fourth (compound **2**) a CAD4 was used. Crystal data for the compounds are summarised in Table I together with details of the refinements. No absorption corrections were applied except for **4** where the crystal was a very thin plate (corrections were: min. 0.569, max. 0.868). For **1**, the non-centrosymmetric space group was chosen on the basis of reflection statistics and inspection of the vector distribution in the Patterson function. All structures were solved by the heavy atom method and refined by the full-matrix least-squares technique based on  $F$ . Hydrogen atoms were placed in calculated positions (C–H, 1.08 Å) with isotropic thermal parameters. Anisotropic thermal motion was assumed for all non-hydrogen atoms. Atom co-ordinates, thermal parameters, full listings of bond distances and angles, as well as  $F_o/F_c$  listings, have been supplied as supplementary material for all four structures together with planes of best fit and intermolecular approaches where appropriate (deposition numbers allocated by the Cambridge Crystallographic Data Centre are CCDC 103323–6 for compounds **1–4**).

## RESULTS

*Crystal Structure of*

*N,N'-1,2-Phenylene-bis(salicylideneiminato)copper(II) · CHCl<sub>3</sub>*

Two crystallographically distinct but structurally similar molecules are found in the asymmetric unit. The copper atoms of the two molecules both exhibit distorted square planar co-ordination geometry with two nitrogen and two oxygen donor atoms. A chloroform molecule is hydrogen bonded to both donor oxygen atoms in each molecule. Thermal ellipsoid diagrams of molecules A and B, showing the numbering system used, are given in Figures 1 and 2 respectively.

*Crystal Structure of*

*N,N'-1,2-Phenylene-bis(salicylideneiminato)copper(II) · 1.25C<sub>5</sub>H<sub>5</sub>N · 0.5H<sub>2</sub>O*

The asymmetric unit contains two structurally distinct complex molecules. One of these, molecule B, has the copper in a slightly distorted square

TABLE I  
Crystal and refinement data for compounds **1**, **2**, **3** and **4**

	Compound <b>1</b>	Compound <b>2</b>	Compound <b>3</b>	Compound <b>4</b>
Empirical formula	$C_{20}H_{14}N_2O_2Cu \cdot CHCl_3$	$C_{25}H_{19}N_3O_2Cu \cdot C_{20}H_{14}N_2O_2Cu \cdot 1.5 (C_5H_5N) \cdot H_2O$	$C_{28}H_{26}N_4O_4Cu$	$C_{17}H_{18}N_2O_8PCu \cdot 4H_2O$
$M_r$	497.3	897.5	546.1	544.9
Crystal colour, shape	brown prism	brown needle	brown prism	green plate
Crystal size/mm	$0.25 \times 0.22 \times 0.15^a$	$0.25 \times 0.22 \times 0.04^b$	$0.25 \times 0.25 \times 0.30$	$0.24 \times 0.20 \times 0.05$
Crystal class	Orthorhombic	Triclinic	Monoclinic	Triclinic
Space group	$Pna2_1$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
$a / \text{\AA}$	20.159(2)	8.748(4)	5.7037(6)	8.697(2)
$b / \text{\AA}$	14.918(1)	14.499(4)	20.394(1)	13.039(3)
$c / \text{\AA}$	13.329(1)	18.725(4)	10.6321(6)	12.418(3)
$\alpha / ^\circ$	90.0	109.93(3)	90.0	110.49(2)
$\beta / ^\circ$	90.0	91.99(1)	101.443(6)	108.61(2)
$\gamma / ^\circ$	90.0	101.64(2)	90.0	63.65(1)

(continued)

TABLE I (cont.)

	Compound 1	Compound 2	Compound 3	Compound 4
$V / \text{\AA}^3$	4008.5	2173.0	1212.2	1159.3
$Z$	8	2	2	2
$F(000)$	2008.0	1002.0	566.0	564.0
Radiation, $\lambda / \text{\AA}$	Cu, 1.5418	Mo, 0.71073	Cu, 1.5418	Cu, 1.5418
$D_c / \text{g cm}^{-3}$	1.65	1.54	1.51	1.62
$\mu (\text{Cu-K}\alpha) / \text{mm}^{-1}$	5.40	1.04	1.64	2.57
$\theta_{\text{max.}} / ^\circ$	67	25	57	52
% decay	< 4	< 1	< 3	< 1
No. of unique data measured	3318	8190	1810	4000
No. of data in refinement ( $I > 3\sigma(I)$ )	2264	5029	1243	2364
No. of parameters refined	523	563	169	278
$R^c$	0.067	0.059	0.046	0.084
$R_w^c$	0.074	0.046	0.071	0.116

<sup>a</sup>Crystal mounted in a capillary with mother liquor.

<sup>b</sup>Crystal fragment mounted in a capillary with mother liquor.

<sup>c</sup> $R = \Sigma(|F_o| - |F_c|) / (\Sigma|F_o|)$ ;  $R_w = [\Sigma w (|F_o| - |F_c|)^2 / (\Sigma w |F_o|^2)]^{0.5}$ . Function minimised =  $\Sigma w (|kF_o| - |F_c|)^2$ .

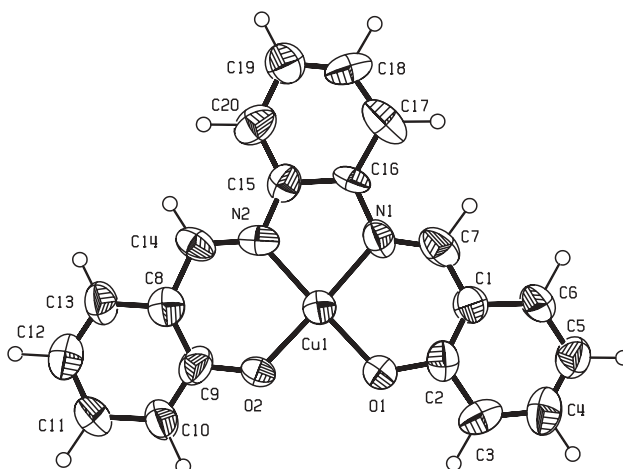


Figure 1. Thermal ellipsoid diagram, at the 50% probability level, for molecule A of the *N,N'*-(1,2-phenylene)bis(salicylideneiminato)copper(II) complex from chloroform (1) showing the numbering system. Hydrogen atoms are numbered according to the carbons to which they are attached.

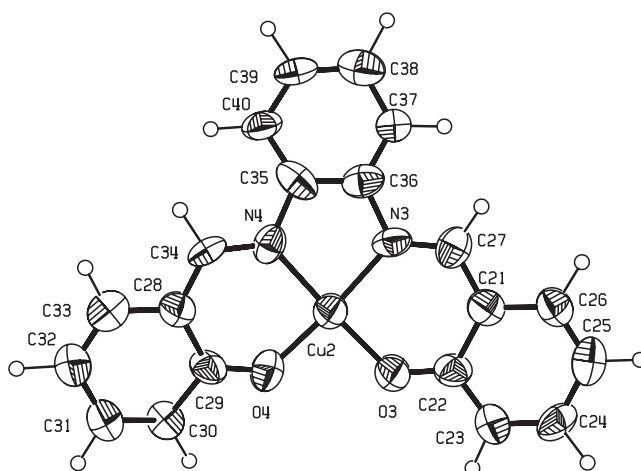


Figure 2. Thermal ellipsoid diagram, at the 50% probability level, for molecule B of the *N,N'*-(1,2-phenylene)bis(salicylideneiminato)copper(II) complex from chloroform (1) showing the numbering system. Hydrogen atoms are numbered according to the carbons to which they are attached.

planar geometry with two oxygen and two nitrogen donors from the ligand. Molecule A has a similarly bound salicylideneiminato ligand but in addition there is also a pyridine molecule in the fifth co-ordination site to give square pyramidal stereochemistry. There is also a water molecule hydrogen bonded

to the two oxygen donors of this complex. In a purely space filling role there are a further 1.5 molecules of pyridine per two complex molecules, one of these lying, in a disordered manner, across a centre of symmetry. Thermal ellipsoid diagrams of molecules A and B, showing the numbering system, are given in Figures 3 and 4 respectively.

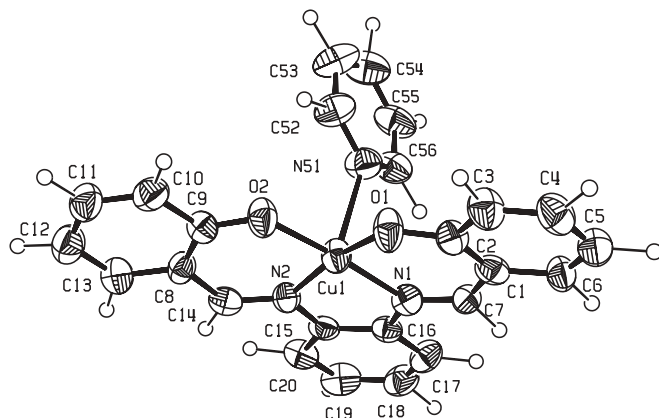


Figure 3. Thermal ellipsoid diagram, at the 50% probability level, for molecule A of the  $N,N'$ -(1,2-phenylene)bis(salicylideneiminato)copper(II) complex from pyridine (**2**) showing the numbering system. Hydrogen atoms are numbered according to the carbons to which they are attached.

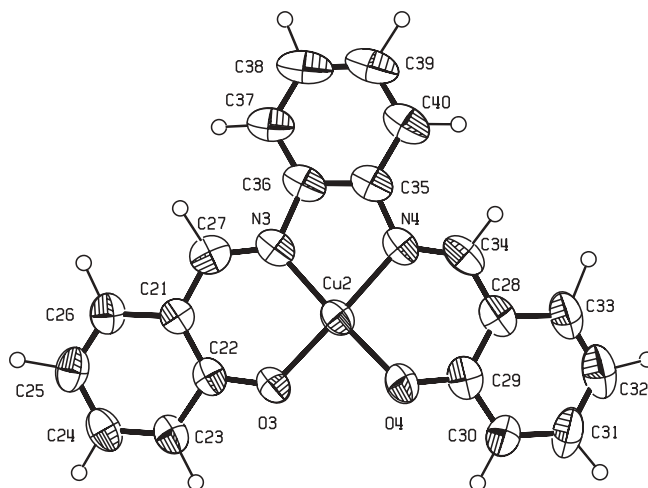


Figure 4. Thermal ellipsoid diagram, at the 50% probability level, for molecule B of the  $N,N'$ -(1,2-phenylene)bis(salicylideneiminato)copper(II) complex from pyridine (**2**) showing the numbering system. Hydrogen atoms are numbered according to the carbons to which they are attached.



*Crystal Structure of Bis(N-phenylpyridoxylideneiminato)copper(II)*

The complex has square planar co-ordination geometry with one copper bound to two bidentate ligands through phenolic oxygen and imine nitrogen atoms. There is no evidence for additional donors in either of the octahedral sites of the copper ion. The latter lies on an inversion centre so that the two pyrim ligands form the *trans* isomer. The chelate and heterocyclic ring of each ligand form an approximately planar moiety but, overall, the complex has the stepped conformation. The two phenyl rings, although planar themselves, lie at angles of  $77.9^\circ$  to the co-ordination plane. A thermal ellipsoid diagram of the molecule showing the numbering system is given in Figure 5.

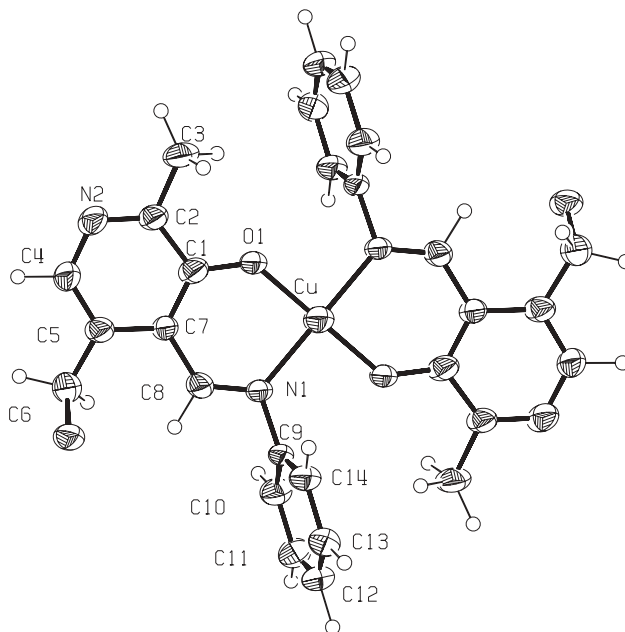


Figure 5. Thermal ellipsoid diagram, at the 50% probability level, for bis(*N*-phenylpyridoxylideneiminato)copper(II) (**3**) showing the numbering system. Hydrogen atoms are numbered according to the carbons to which they are attached.

*Crystal Structure of  
Aqua(5-phosphopyridoxylidene-DL-phenylalanineato)copper(II)*

This is a re-appraisal of a previously investigated structure.<sup>20,21</sup> Square pyramidal co-ordination geometry is observed for the copper atom with three co-ordination sites being occupied by donor atoms from the pyrim ligand. These are the phenolic oxygen, the imine nitrogen and the carboxyl

oxygen. The fourth planar position is occupied by a water molecule and the apical position by a phosphate oxygen of an adjacent molecule. A thermal ellipsoid diagram of the molecule showing the numbering system is given in Figure 6.

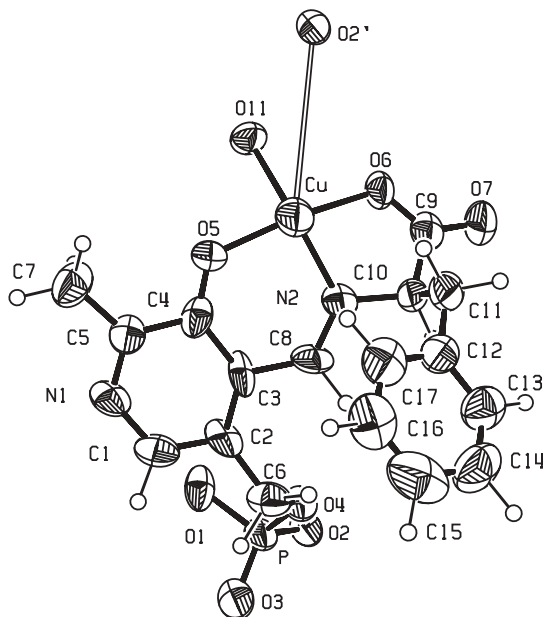


Figure 6. Thermal ellipsoid diagram, at the 50% probability level, for aqua(5'-phosphopyridoxylidene-DL-phenylalanineato)copper(II) (**4**) showing the numbering system. Hydrogen atoms are numbered according to the carbons to which they are attached.

## DISCUSSION

Compound **1** reveals a chloroform hydrogen-bound to both oxygen donors of each of the two independent molecules in the crystal. The H...O distances of 2.3 to 2.4 Å and the geometry of the arrangements confirm the interaction.<sup>23</sup> Compound **2** differs in having no such hydrogen bonding. Molecule A has a pyridine co-ordinated to copper but molecule B has no solvent interaction even though further pyridine and water molecules are present in the crystal. »Edge on« line diagrams are presented in Figure 7 to highlight the molecular distortions from overall planarity.

The four different molecules represent, in somewhat exaggerated form, the four conformational possibilities noted by Suresh *et al.*<sup>24</sup> as being found in this complex with copper(II) and a monoclinic form of cobalt(II) – essen-

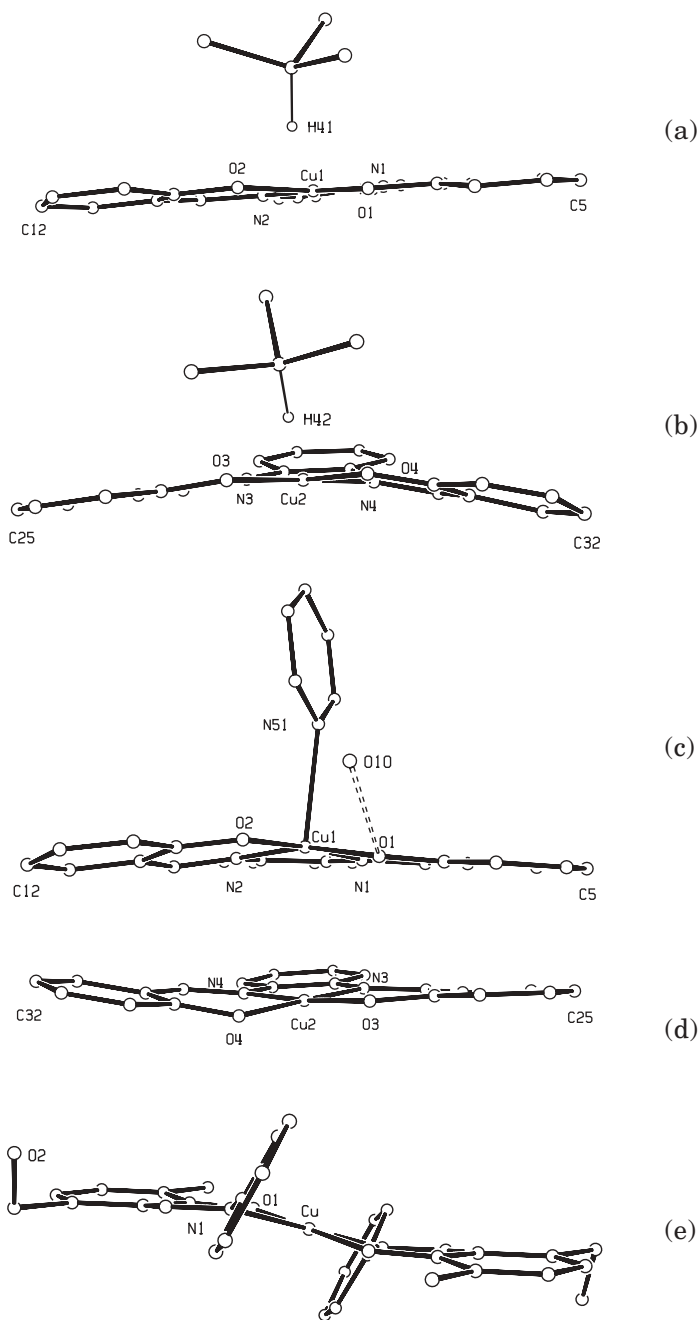


Figure 7. Edge-on line diagrams of compounds **1**, **2** and **3**: (a) molecule A from chloroform, (**1**); (b) molecule B from chloroform, (**1**); (c) molecule A from pyridine, (**2**); (d) molecule B from pyridine, (**2**); (e) bis(*N*-phenyl-pyridoxylideneiminato)copper(II) (**3**).

tially planar with a very small tetrahedral distortion – and again with cobalt(II) – umbrella shaped in both the orthorhombic four co-ordinate form and with square pyramidal five co-ordination. On the question of the contribution of electronic and steric effects to the overall molecular configuration answers remain elusive. We are presented with a further instance of the same complex molecule taking up slightly different conformations in the presence of solvents which not only impose packing requirements but which also, in three of the molecules, have further bonding influences as well.

Molecule A of compound **1** is nearly planar overall with the benzene ring C1–C6 being almost co-planar with the co-ordination plane O1, O2, N1, N2. (The distances of atoms from the mean plane through the four donors are listed in Supplementary Data Table IX together with the dihedral angles which can be defined in the molecule.) In particular the angle between planes 4 (O1,N1,C1,C2,C7) and 6 (Cu,O1,N1) is only  $0.7^\circ$  whereas that between the corresponding planes in the other salicylaldimine residue is minus (the sign is arbitrary)  $4.5^\circ$ . The angle between 1 and 4 *{i.e.}* (C1,C2,C3,C4,C5,C6) and (O1,N1,C1,C2,C7) is  $0.6^\circ$  and between 2 and 5 *{i.e.}* (C8,C9,C10,C11,C12,C13) and (O2,N2,C8,C9,C14) it is  $2.7^\circ$ . Unfortunately these could not be directly compared with the corresponding angles in the unsolvated crystal<sup>24</sup>, the atom co-ordinates not being immediately available, but the text mentions an angle, in both crystallographically independent molecules, of  $3^\circ$  between one benzene ring and the mean co-ordination plane (which includes the Cu atom) and an angle of  $60^\circ$  (*sic*) with the other. If this latter figure is taken as  $6^\circ$  then the comparison with molecule A of the  $\text{CHCl}_3$  solvate is with  $2.2^\circ$  and  $5.5^\circ$ .

It has been postulated that hydrogen bonding to donor oxygen atoms in these types of complexes encourages overall molecular planarity<sup>5</sup> so it is interesting that in molecule A the  $\text{CHCl}_3$  which forms a bifurcated hydrogen bond to the two donor oxygens is marginally closer to O1; but whether or not this accounts for the near planarity of the related salim group is not clear. What is also unclear is the significance of the slight chair conformation evident in this phenyl ring from Figure 7. Atoms C1, C3, C4, C6 do not deviate by more than  $0.005 \text{ \AA}$  from their mean plane but C2 is  $+0.087$  and C5 is  $-0.067 \text{ \AA}$  therefrom. Although by no means unknown in other salim complexes<sup>5</sup> we can do no more in a structure for which  $R = 0.067$  than note the matter.

Molecule B of the  $\text{CHCl}_3$  solvate also has a bifurcated hydrogen bond to the donor oxygens. The  $\text{C}(\text{CHCl}_3)\cdots\text{O}$  distances suggest that the bond may be fractionally weaker, by about  $0.1 \text{ \AA}$ , than in A. What is clear is that the complex is much less planar with the angles between the salim benzene rings and the co-ordination plane being  $6.7^\circ$  and  $12.9^\circ$  both being tipped in

the sense which gives an umbrella conformation. As a consequence, if trigonal bonding is to be maintained about the nitrogen donors, the phenylene ring is tipped in the opposite direction. Molecule B is, in fact, more akin to a reported cobalt(II) complex<sup>24,25</sup> in its orthorhombic form than to the unsolvated copper complex.<sup>24</sup> As with the latter complex, however, there are slight tetrahedral distortions in the molecules of compound **1** as can be seen from the deviations from the mean co-ordination planes and Figure 7. There are also deviations from the overall planarity of the phenyl ring C28, C29, C30, C31, C32, C33 but this time describing an envelope. The deviations from the mean plane through C29, C30, C31, C32 do not exceed 0.007 Å whereas C28 is 0.111 and C33 is 0.063 Å therefrom. None of the other phenyl groups in **1** deviate by more than 0.01 Å from overall planarity.

Molecule B of the complex crystallised from pyridine is unsolvated even though the crystal contains two and a half pyridines and one water molecule per two molecules of complex. By contrast molecule A has a co-ordinated pyridine in the apical position of copper and also has the water molecule hydrogen-bonded to one of its donor oxygens. In B the angles between the mean planes through the benzene rings of the salim groups and the co-ordination plane are 6.9° and 14.0° but the line diagram of Figure 7d and the deviations from the co-ordination plane show that the molecule also has a slight tetrahedral twist with one salim »wing« more or less planar with the co-ordinated atoms but with the other wing tipped away. In this respect this unsolvated molecule is not unlike molecule A of the CHCl<sub>3</sub> adduct.

Molecule A of the pyridine solvate is not much different. If the copper atom is omitted from the calculated donor mean plane, then the angles with the benzene planes of the salim wings are 4.0° and 11.3°. It is pertinent, in this respect, to note that molecule A has a water hydrogen-bonded to the oxygen donor (O1) of the more planar salim group.

The four new structures show considerable flexibility. Exact conformations, as a balance between packing and molecular bonding forces, are complicated by charge transfer interactions which, in themselves, are also a balance between electronic and steric effects. All the molecules of compounds **1** and **2**, except those with pyridine bonded to copper, are stacked in various ways indicative of charge transfer interactions. This is also a feature of the arrangement in the unsolvated crystal<sup>24</sup> and is seen as a way of meeting the tendency for copper in square planar complexes to extend its co-ordination sphere. In terms of earlier suggestions it reflects the fact that the ligand field of the donors needs strengthening although these molecules do not form dimers through oxygen bridges as commonly occurs. The related complex *N,N'*-dimethylene-bis(salim)Cu(II) is such a dimeric example.<sup>26,27</sup> The intermolecular contacts in each of the relevant molecules demonstrate the closeness of the approaches which are made.

Lastly, in this survey of the four molecules, a comparison between bond lengths and conformation was made. The accurate bond distances found in the 2:1 charge transfer complex between *N,N'*-1,2-phenylene-bis(salim)Cu(II) and 7,7,8,8-tetracyanoquino-dimethane<sup>28</sup> are taken as reference. The latter accord with the general observation that the benzene rings of the salim groups show three consecutive longer (than expected for benzene) and three shorter bonds, that bonds of the type C1–C7 and O1–C2 (see Figure 1) are about 0.03 Å shorter than in the free ligand and that a lengthening of the N1–C7 type of bond, which has been postulated,<sup>25</sup> does not occur.

Unfortunately the accuracy of the bonds determined for the CHCl<sub>3</sub> solvate (e.s.d's  $\approx$  0.02 Å) does not justify detailed comparison but the molecules in the pyridine solvate (e.s.d's  $\approx$  0.008 Å) are more accurately defined. With one exception, namely N3–C27 = 1.330 Å, the bonds of the type O1–C2, C1–C7, N1–C7 compare well with those found in the 2:1 adduct. The benzene rings of the salim groups also show the long bond, short bond, pattern with the exception that the middle »short« bonds measures 1.420(8), 1.403(8), 1.396(8) and 1.42(1) Å. The increased length, accords with the view that co-ordination reinforces the ketamine over the enolimine form of the ligand.<sup>25</sup> The ketamine contribution would also suggest a lengthening of the nitrogen to phenylene bonds. One such bond in each molecule is *ca.* 0.03 Å longer than the other; N1–C16 = 1.414(6), N2–C15 = 1.452(6), N3–C36 = 1.442(7), N4–C35 = 1.411(7) Å. Why a lengthening in one and not both bonds or why a lengthening in only N3–C27 and not the three other N–C bonds of the imino type are pertinent questions.

Complex **3** has a classic square planar stereochemistry with the copper atom on a crystallographic centre of symmetry. The molecule is »stepped« the copper atom being 0.33 Å from the plane through a pyridine ring. The angle between the plane through Cu, O1, N1 and the pyridine ring is 15.2°; through Cu, O1, N1 and the chelate ring O1, N1, C1, C7, C8 it is 14.6° and between the pyridine and chelate rings 5.7°. These numbers indicate a small »twist« of the pyridine ring with respect to the chelate ring and this can be visualised from the observation that the five atoms N2, C2, C4, C5, C7 of the pyridine ring are almost co-planar (largest deviation 0.006 Å) with the sixth, C1, lying 0.06 Å from the plane. There are no solvent molecules in the crystal but there is one inter-molecular hydrogen bond from the hydroxy group to the pyridine nitrogen. The internal ring angle of 119.9° suggests hydrogen bonding at this atom and this was confirmed by the location of appropriately placed electron density. The N2...O2' distance is 2.755(5) Å.

Within the pyridine ring there is again the three short, three long, bond sequence seen in the salim series. The C–O phenolic bond is similarly short and the N=C imine bond also remains unchanged from expectation. But the bond from the pyridine ring to the imino carbon is, at 1.449(7) Å, up to 0.02

Å longer than observed in some salim complexes and close to the length seen in uncomplexed ligands. The same situation tends to occur in many of the pyrim copper(II) complexes we have monitored and presumably represents an electronic change. Averaging the observed bond lengths for twelve salim and six pyrim measurements for which the standard deviations are better than 0.01 Å gives the figures of Table II. The situation could be described in terms of an enhancement in the pyrim series of the enolimine system mentioned earlier, although noting that the C–O enol bonds are almost identical in both series at approximately 1.30 Å. An enhanced enolimine form suggests that electron delocalisation from the pyridine ring does not extend to the donor nitrogen in the way supposed for salim complexes. Pyridine ring substitution is, instead, more likely to influence bonding at the oxygen rather than nitrogen donors and therefore to have less effect on the planar/tetrahedral geometry adopted at the copper. Thus the planar electronic influence which, it is claimed, is exerted by a methyl substituent in the 3-position on a salim ring<sup>5</sup> is not seen in the partially tetrahedral complex bis(*N-t*-butyl-pyrim)Cu(II)<sup>29</sup> even though there is a methyl in the equivalent position on the pyridoxal.

Another interesting comparison can be made between the two series when the R-group on the nitrogen donors is, respectively, phenyl, benzyl and phenylethyl. For both the salim<sup>30</sup> and the pyrim series (compound **3**) the molecules are planar when R is phenyl. In the latter series the complex containing a benzyl R-group is partially tetrahedral<sup>31</sup> whereas that with phenylethyl is again planar.<sup>32</sup> In a modified salim series with a methyl substituent on the imine carbon, *i.e.* with the ligand based on *o*-hydroxy acetophenone, the *N*-benzyl and *N*-phenylethyl complexes are both tetrahedral.<sup>33</sup> It can be postulated for the pyrim compounds, and the exact molecular arrangement gives support, that the methylene carbon of the benzyl group, contrary to the action of the phenylethyl group, is stabilised by its phenyl and can load electron density onto the nitrogen donors to bring about a tetrahedral stereochemistry. But when the R-group is phenyl it cannot make such a contribution because of its rotation, by 77.9°, out of the plane of the complex. The unexpected tetrahedral nature of the complex based on *o*-hydroxyacetophenone when phenylethyl is the R-group arises, it has been argued with some supporting evidence,<sup>5</sup> from the action of the methyl substituent on the imine carbon.

As reported earlier complex **4** joins a number of other pyridoxylidene-amino acid ligands in being tridentate towards copper(II) binding through the usual oxygen and nitrogen donors and an oxygen of the amino-acid carboxylic group. The metal ion in all these complexes adopts a square pyramidal stereochemistry, the remaining two positions being occupied by water

TABLE II  
Comparison of selected bond lengths / Å

Compound <sup>a</sup>	N1–C7	C1–C7	O1–C2	C2–C3	C3–C4	C4–C5	C5–C6	C1–C6	C1–C2
ensalim <sup>b</sup>	1.270(3)	1.457(4)	1.345(3)	1.393	1.372	1.392	1.376	1.393	1.412
ophensalim <sup>c</sup>	1.288	1.449	1.345	1.401	1.384	1.392	1.389	1.406	1.420
salimCu(II) <sup>d</sup>	1.293(5)	1.434(4)	1.305(3)	1.420(4)	1.369(3)	1.396(4)	1.366(3)	1.412(3)	1.419(4)
Compound <sup>e</sup>	N1–C8	C7–C8	O1–C1	C1–C2	C2–N2	N2–C4	C4–C5	C5–C7	C1–C7
pyrimCu(II) <sup>f</sup>	1.283(5)	1.445(3)	1.307(1)	1.433(2)	1.324(5)	1.364(6)	1.364(4)	1.424(3)	1.402(2)

<sup>a</sup>Atom identification as in Figure 1.

<sup>b</sup>*N,N'*-Dimethylenebis(salicylideneimine) Ref. 36 (not all e.s.ds. reported).

<sup>c</sup>*N,N'*-*o*-Phenylenebis(salicylideneimine) Ref. 24 (mean e.s.ds. reported: C–C 0.007, C–N(O) 0.006 Å).

<sup>d</sup>Average of 12 independent values in salim complexes, Refs. 15, 26, 27, 37, and compounds **1**, **2**.

<sup>e</sup>Atom identification as in Figure 6.

<sup>f</sup>Average of 6 independent values in pyrim complexes, Refs. 28, 30, 31, and compound **3**.



and an oxygen nitrogen of a neighbouring molecule although in the complex where histamine replaces histidine the two additional co-ordination sites are occupied by chloride ions.<sup>34</sup> In **4** a water occupies the fourth in-plane position and an oxygen of a neighbouring phosphate takes the apical site. The molecular structure is the same as that reported<sup>21</sup> and the copper-donor bond lengths statistically identical. The crystal structure is also essentially the same (the less conventional cell reported for the film data has been retained) except that four water molecules per complex have been located in a slightly larger cell instead of the 2.5 reported. Occupancy factors were refined for the water but none fell to less than 0.89. All four, as well as the coordinated water, are involved with the carboxylate oxygens, the pyridine ring nitrogen, the phenolic oxygen and three phosphate oxygens in an extensive, three-dimensional, hydrogen bonding network throughout the crystal.

A comparison of bond lengths in **4** with those in the complex (pyridoxylidene-DL-valinato)copper(II)<sup>35</sup> is interesting. It has previously been suggested that the electronic ground state of the latter, seen in bond changes favouring the ketamine contributor of Figure 4 of the reference, predisposes it toward reactivity. Complex **4**, on the other hand, has bond lengths which favour the enolimine form and other pyridoxylidene complexes incorporating an amino-acid into the ligand are similar. The distinguishing feature in the valinato compound is the co-ordination of the pyridine nitrogen which, it is assumed, then stabilises the negative charge on this atom as the canonical contributor presupposes. This nitrogen is hydrogen bound in a number of the amino-acid compounds, including **4**, but this interaction evidently does not induce the electron distribution seen in the valine analogue. Of particular importance in predisposing **4** for reactivity is said to be the stabilisation of charge on the imino group by  $\pi$ - $\pi$  interaction with the phenyl of the amino-acid<sup>21</sup> the intra-molecular distances being of the order of 3.1 Å.

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## SAŽETAK

## Kompleksi Schiffovih baza s bakrom(II)

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Opisuju se četiri kristalne i molekulske strukture kompleksa bakra sa Schiffovim bazama. U slučaju jedne radi se o ponovnom utočnjavanju strukture o kojoj je već ranije izvješćeno. Kristali *N,N'*-1,2-fenilen-bis(salicilideniminato)-bakra(II) priređeni su iz dva različita otapala, kloroforma i piridina. Kristali izrasli iz kloroforma pripadaju rompskom sustavu, prostornoj grupi  $Pna2_1$  s parametrima jedinične ćelije:  $a = 20,159(2)$ ,  $b = 14,918(1)$ ,  $c = 13,329(1)$  Å. U asimetričnoj jedinki nalaze se dvije kristalografski različite molekule s kvadratno koordiniranim atomom bakra. Kristalizacijom iz piridina nastaju trikliniski kristali s parametrima jedinične ćelije:  $a = 8,748(4)$ ,  $b = 14,499(4)$ ,  $c = 18,725(5)$  Å,  $\alpha = 109,93(3)$ ,  $\beta = 91,99(2)$ ,  $\gamma = 101,64(3)^\circ$ . U asimetričnoj jedinki prostorne grupe  $P\bar{1}$  nalaze se dvije, stereokemijski različite molekule, jedna s kvadratno koordiniranim atomom metala, a druga s bakrovim atomom kvadratno-piramidne koordinacije, s molekulom piridina u apikalnom položaju. Bis(*N*-fenilpiridoksilideniminato)bakar(II) kristalizira u monoklinskoj ćeliji s parametrima:  $a = 5,7037(6)$ ,  $b = 20,394(1)$ ,  $c = 10,6321(6)$  Å,  $\beta = 101,443(6)^\circ$  i prostornom grupom  $P2_1/c$ . Bakrov atom kvadratne je koordinacije s kisikovim odnosno dušikovim atomima u *trans*-položaju. Ponovnim utočnjavanjem strukture kompleksa akva(5-fosfopiridoksiliden-D,L-fenilalaninato)bakra(II) potvrđeno je kvadratno-piramidno okruženje bakra s dva kisikova i jednim dušikovim donornim atomom iz kelatnog liganda te jednom molekulom vode dok apikalni položaj zauzima fosfatni kisikov atom susjedne molekule. Kristali su trikliniski, prostorne grupe  $P\bar{1}$ , s parametrima elementarne ćelije:  $a = 8,697(2)$ ,  $b = 13,039(3)$ ,  $c = 12,418(3)$  Å,  $\alpha = 110,49(2)$ ,  $\beta = 108,61(2)$ ,  $\gamma = 63,65(10)^\circ$ .