Metal Complexes of Vitamin B_6 Related Compounds. Crystal and Molecular Structures of Aqua(5′-phosphopyridoxylideneglycinato)copper(II) Trihydrate and Bis(pyridoxylideneglycinato)nickel(II) Hexahydrate†

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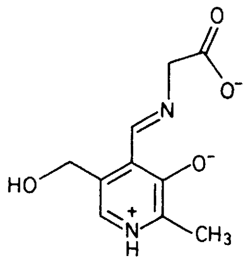
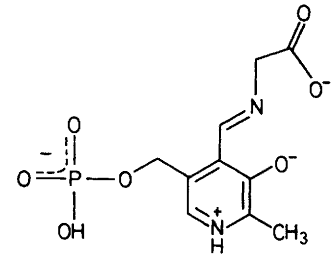
The crystal structures of two Schiff-base metal complexes, aqua(5′-phosphopyridoxylideneglycinato)-copper(II) trihydrate, $[Cu(P\text{-}Pxd\text{-}Gly)(H_2O)]\cdot3H_2O$ (**1**), and bis(pyridoxylideneglycinato)nickel(II) hexahydrate, $[Ni(Pxd\text{-}Gly)_2]\cdot6H_2O$ (**2**), have been determined using single-crystal *X*-ray diffraction methods. Compound (**1**) crystallizes in space group $P\bar{1}$ with $a = 8.394(4)$, $b = 9.819(8)$, $c = 10.884(7)$ Å, $\alpha = 101.85(6)$, $\beta = 97.48(5)$, $\gamma = 112.60(5)°$, and $Z = 2$; compound (**2**) crystallizes in space group *Pnna* with $a = 20.233(3)$, $b = 19.423(3)$, $c = 13.956(3)$ Å, and $Z = 8$. The structures were solved by the heavy-atom method and refined to *R* values of 0.064 and 0.129 respectively. The Cu^{II} ion has a square-pyramidal geometry in compound (**1**) with phenolic oxygen, imine nitrogen, and carboxylate oxygen atoms of the Schiff-base ligand and a water molecule as basal donors. The compound is a one-dimensional polymer due to the axial co-ordination of one of the phosphate oxygens of a neighbouring molecule. The two tridentate Schiff-base ligands provide an octahedral geometry around the Ni^{II} ion in compound (**2**). The near-planarity of the ligand in compound (**1**) and non-planarity in compound (**2**) are discussed in terms of the relative reactivities.

Pyridoxal 5′-phosphate (PLP) is a coenzyme which plays an important role in the metabolic reactions of amino acids such as transamination, decarboxylation, β-elimination, and racemization. Most of these reactions can be mimicked in non-enzymatic systems, where metal ions are often needed to promote such reactions. The role of metal ions and the vitamin B_6 group of compounds, together with their analogues and homologues, in the catalysis of these reactions have been extensively reviewed.[1] It is believed that the metal ions simulate some of the features of enzymatic active sites by acting as a trap for the Schiff base formed between pyridoxal (PL) and the amino acid and, more importantly, by labilizing the bonds adjacent to the co-ordinating groups of the amino acid moiety. Though these reaction intermediates have been well studied in several solution systems[2] and some complexes are characterized in the solid state,[3,4] *X*-ray structural studies on such complexes are not numerous. *X*-Ray investigations on 1:1 and 1:2 metal–pyridoxylideneamino acid complexes[5–8] have confirmed the ligating sites predicted from solution studies and have enabled structure–reactivity patterns to be deduced. Further, it has been observed that the efficiency of the catalytic behaviour varies for different metal ions[9] and it is believed that this fact may be related to structural differences.

We have undertaken a programme of studies on the syntheses and structural characterization of transition metal complexes of Schiff bases involving PL or PLP and amino acids. We report here the crystal and molecular structures of the copper(II) complex of 5′-phosphopyridoxylideneglycinate (*P*-Pxd-Gly), $[Cu(P\text{-}Pxd\text{-}Gly)(H_2O)]\cdot3H_2O$ (**1**) and the nickel(II) complex of pyridoxylideneglycinate (Pxd-Gly), $[Ni(Pxd\text{-}Gly)_2]\cdot6H_2O$ (**2**). A comparison of the two structures is also made.



Pxd-Gly



P-Pxd-Gly

Experimental

The syntheses of the complexes (**1**) and (**2**), together with several others, and some of their properties will be published elsewhere.[3] Compound (**1**) was crystallized from an aqueous solution of $Cu(Gly)_2\cdot H_2O$ and PLP (1:1). Compound (**2**) crystallized out when acetone was diffused into a water-methanol (1:1) solution of $NiCl_2\cdot6H_2O$, PL, and Gly (1:2:2).

X-*Ray Data Collection.—Compound* (**1**). One hemisphere of intensity data ($+h$, $\pm k$, $\pm l$) was collected by using the $\omega/2\theta$ scan technique on a Syntex $P2_1$ automated four-circle diffractometer. A variable scan speed was employed with lower and upper limits of 2.5 and 12.5° min^{-1} respectively.

Compound (**2**). Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer by $\omega/2\theta$ scan with a scan speed of 10° min^{-1} and scan width of $\Delta\theta = (0.75 + 0.45 \tan\theta)$.

The data were corrected for Lorentz and polarisation effects but not for absorption. Crystal data and summary of data collection and structure refinement are given in Table 1.

Structure Determination and Refinement.—Compound (**1**). The structure was solved by the heavy-atom technique and

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† *Supplementary data available* (No. SUP 56251, 11 pp.): thermal parameters, H-atom co-ordinates, least-squares planes. See Instructions for Authors. *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

refined by full-matrix least-squares treatment with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms, five out of 11 being located from a difference Fourier map and the rest from geometrical considerations, were included in subsequent calculations with their thermal parameters set equal to 0.019 + $U_{iso.}$ of the heavy atom to which they were bonded. The quantity minimised during refinement was $w[|F_o| - |F_c|]^2$ where $w = 1.557/[\sigma^2(F_o) + 0.000\,42|F_o|^2]$. The positional parameters are given in Table 2. Selected bond distances and angles are summarized in Table 3.

Compound (**2**). A three-dimensional Patterson synthesis helped to locate the position of the nickel atom. However, the identification of the other atoms was not straightforward due to the peculiar position of the heavy atom (0.16, 0.25, 0.0). As a result, the contribution of the heavy atom to the structure factor is restricted only to those *hkl* reflections where both *h* and *l* are even. In the nickel-atom phased (R = 0.46) difference Fourier map six pairs of peaks were seen around the nickel atom at distances of 1.9—2.1 Å. In every pair, the two peaks were separated by a distance of *ca.* 1.2 Å. Two sets of six peaks (one each from every pair) corresponded to an approximate octahedral co-ordination. Both difference Fourier maps including each of the two sets of six atoms revealed positions corresponding to two chelate rings of one of the ligands. However, one of the maps, which revealed additional atoms corresponding to the pyridine ring of the ligand and where interpeak distances were chemically more reasonable, was chosen for refinement, resulting in an R value of 0.25. A subsequent difference Fourier map revealed the rest of the atoms. The oxygen atom, O(2) of the hydroxymethyl group and one of the water molecules, O(W5) showed split peaks and hence were refined with partial occupancies. Hydrogen atoms were fixed from geometric considerations. The best results were obtained using unit weights and the refinement converged to a conventional R of 0.129. The positional parameters for the non-hydrogen atoms are given in Table 4. Selected bond distances and angles are listed in Table 5.

The program SHELX 76[10] was used for the structure solution and refinement. The scattering factors for H, C, N, O, and P atoms were used as available in the SHELX program and for Cu and Ni they were taken from International Tables.[11] The molecular structure and the packing diagrams were drawn using the ORTEP-II program.[12]

Table 1. Crystal data

Compound	(**1**)	(**2**)
Formula	$C_{10}H_{19}CuN_2O_{11}P$	$C_{20}H_{34}N_4NiO_{14}$
M	439.7	613.2
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pnna*
a/Å	8.394(4)	20.233(3)
b/Å	9.819(8)	19.423(3)
c/Å	10.884(7)	13.956(3)
α/°	101.85(6)	90
β/°	97.48(5)	90
γ/°	112.60(5)	90
U/Å^3	788.5	5 484.6
Z	2	8
D_m/Mg m^{-3}	1.81	1.48
D_c/Mg m^{-3}	1.85	1.483
F(000)	430	2 650
μ(Mo-K_α)/cm^{-1}	15.45	7.37
λ(Mo-K_α)/Å	0.7107	0.7107
Crystal size (mm)	0.05 × 0.08 × 0.38	0.15 × 0.23 × 0.25
2θ range (°)	4—55	0—50
No. of reflections measured	3 085	3 562
No. of unique reflections [$I \geqslant 3\sigma(I)$]	1 464	1 857
$R\ [= \Sigma\|F_o - \|F_c\|\|/\Sigma F_o]$	0.064	0.129
$R'\ \{= [\Sigma w(F_o - \|F_c\|)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$	0.070	0.131
Largest peaks in final difference maps (e Å^{-3})	0.21	0.35

Results

The molecular structures of the compounds (**1**) and (**2**) with the atom numbering scheme are shown in Figures 1 and 2 respectively.

Compound (**1**).—[Cu(*P*-Pxd-Gly)(H$_2$O)]·3H$_2$O has 1:1 stoicheiometry and the *P*-Pxd-Gly Schiff base acts as a bridging ligand between two Cu^{II} ions; it is tridentate with respect to one metal and monodentate with respect to the other. The Cu^{II} ion has an approximate square-pyramidal geometry. The phenolic oxygen O(1), imine nitrogen N(2), and carboxylate oxygen O(3) of the Schiff base and a water molecule O(W1) constitute the square base, while one of the phosphate oxygens of a neighbouring molecule O(5′) occupies the axial site. This results in a zigzag chain of molecules running along the crystallographic *a* axis (Figure 3). The equatorial bond lengths are in the range 1.902—1.968 Å, whereas the axial bond length is 2.317 Å. The *cis* bond angles in the plane range from 84.6 to 92.8° and the *trans* angles are 170.0 and 165.6°. The Cu–O(5′) bond is nearly perpendicular to the square plane with the angles, O(5′)–Cu–(basal donor) ranging from 95.2 to 99.3°. The four basal atoms show small but significant tetrahedral deviations (0.035—0.040 Å) from the least-squares plane through these atoms.

The co-ordinated ligand is made of three rings, one heterocyclic and two chelate. The heterocyclic ring (I) is planar, the largest deviation from the best plane being 0.02 Å for C(3). The chelate rings are much less planar, the six-membered ring (II)

Table 2. Fractional atomic co-ordinates (× 10^4) for non-hydrogen atoms in (**1**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
Cu	2 700(1)	816(1)	466(1)
N(1)	2 492(11)	4 267(10)	4 757(7)
C(1)	2 827(13)	3 133(11)	4 153(9)
C(2)	2 386(13)	2 625(11)	2 769(10)
C(3)	1 621(13)	3 403(11)	2 123(9)
C(4)	1 228(13)	4 577(11)	2 820(9)
C(5)	1 688(14)	4 989(11)	4 145(9)
C(6)	3 662(15)	2 392(13)	4 921(10)
C(7)	1 206(14)	3 034(12)	710(10)
C(8)	357(13)	5 419(11)	2 160(10)
O(1)	2 748(10)	1 524(8)	2 239(6)
O(2)	−1 328(9)	4 349(8)	1 282(6)
N(2)	1 546(10)	2 053(9)	−29(8)
C(9)	1 085(14)	1 775(12)	−1 434(9)
C(10)	1 455(15)	452(13)	−2 133(10)
O(3)	2 205(10)	−117(8)	−1 404(6)
O(4)	1 027(12)	20(9)	−3 300(7)
P	−3 087(4)	3 603(3)	1 803(3)
O(5)	−4 457(9)	2 591(8)	592(6)
O(6)	−2 672(10)	2 657(8)	2 685(7)
O(7)	−3 396(10)	4 853(8)	2 621(6)
O(W1)	3 247(11)	−792(8)	879(7)
O(W2)	5 396(13)	3 544(10)	−1 725(8)
O(W3)	4 246(14)	−975(11)	3 245(8)
O(W4)	1 234(17)	−1 523(11)	4 449(10)

Table 3. Bond lengths (Å) and angles (°) with e.s.d.s for compound (**1**). Primed atoms are related to unprimed atoms by unit translation along the *a* axis

Cu–O(1)	1.902(7)	C(1)–C(2)	1.44(1)	C(4)–C(5)	1.37(1)	C(10)–O(4)	1.21(1)
Cu–N(2)	1.935(9)	C(1)–C(6)	1.49(2)	C(4)–C(8)	1.52(2)	P–O(2)	1.611(9)
Cu–O(2)	1.968(6)	C(2)–C(3)	1.40(2)	C(8)–O(2)	1.45(1)	P–O(5)	1.496(7)
Cu–O(W1)	1.924(8)	C(2)–O(1)	1.28(1)	C(7)–N(2)	1.27(1)	P–O(6)	1.560(8)
Cu–O(5′)	2.317(8)	C(3)–C(4)	1.42(2)	N(2)–C(9)	1.47(1)	P–O(7)	1.491(8)
N(1)–C(1)	1.32(1)	C(3)–C(7)	1.47(1)	C(9)–C(10)	1.53(2)		
N(1)–C(5)	1.36(1)			C(10)–O(3)	1.29(1)		

O(1)–Cu–N(2)	92.3(4)	N(1)–C(1)–C(6)	119(1)	C(1)–C(2)–C(3)	117(1)	Cu–O(1)–C(2)	128(1)
O(1)–Cu–O(3)	170.0(3)	C(2)–C(1)–C(6)	121(1)	C(1)–C(2)–O(1)	117(1)	C(8)–O(2)–P	121(1)
O(1)–Cu–O(W1)	87.9(3)	Cu–N(2)–C(7)	127(1)	C(3)–C(2)–O(1)	126(1)	Cu–O(3)–C(10)	116(1)
N(2)–Cu–O(3)	84.6(3)	Cu–N(2)–C(9)	112(1)	C(2)–C(3)–C(4)	121(1)	O(2)–P–O(5)	102.9(4)
N(2)–Cu–O(W1)	165.6(3)	C(7)–N(2)–C(9)	120(1)	C(2)–C(3)–C(7)	121(1)	O(2)–P–O(6)	106.0(4)
O(3)–Cu–O(W1)	92.8(3)	N(2)–C(9)–C(10)	111(1)	C(4)–C(3)–C(7)	118(1)	O(2)–P–O(7)	109.3(4)
O(1)–Cu–O(5′)	95.2(3)	C(9)–C(10)–O(3)	116(1)	C(3)–C(4)–C(5)	119(1)	O(5)–P–O(6)	112.0(5)
N(2)–Cu–O(5′)	95.0(3)	C(9)–C(10)–O(4)	119(1)	C(3)–C(4)–C(8)	123(1)	O(5)–P–O(7)	118.1(5)
O(2)–Cu–O(5′)	94.5(3)	O(3)–C(10)–O(4)	126(1)	C(5)–C(4)–C(8)	119(1)	O(6)–P–O(7)	107.8(5)
O(W1)–Cu–O(5′)	99.3(3)			N(1)–C(5)–C(4)	120(1)	Cu–O(5′)–P′	126.2(4)
C(1)–N(1)–C(5)	124(1)			C(3)–C(7)–N(2)	125(1)		
N(1)–C(1)–C(2)	120(1)			C(4)–C(8)–O(2)	111(1)		

Table 4. Fractional atomic co-ordinates (× 10^4) for non-hydrogen atoms in compound (**2**) with e.s.d.s in parentheses. Primed atoms are related to unprimed atoms by a pseudo-two-fold axis

Atom	*x*	*y*	*z*
Ni	1 690(1)	2 500(2)	−46(2)
N(1)	4 128(7)	2 548(10)	−1 333(11)
C(1)	3 504(14)	2 214(13)	−1 305(16)
C(2)	2 921(10)	2 616(10)	−1 026(15)
C(3)	3 068(13)	3 279(12)	−685(17)
C(4)	3 719(13)	3 564(15)	−711(19)
C(5)	4 212(12)	3 188(12)	−1 051(17)
C(6)	3 474(17)	1 462(14)	−1 623(26)
C(7)	2 577(12)	3 724(11)	−178(30)
C(8)	3 888(16)	4 286(15)	−465(23)
O(1)	2 396(7)	2 277(8)	−1 007(11)
O(2)[a]	3 548(18)	4 772(18)	−1 071(27)
O(21)[b]	4 486(35)	4 590(37)	−666(53)
N(2)	2 024(8)	3 491(8)	63(16)
C(9)	1 453(17)	3 955(18)	319(25)
C(10)	1 085(12)	3 534(14)	1 080(22)
O(3)	1 065(8)	2 879(7)	1 009(12)
O(4)	724(8)	3 860(9)	1 703(13)
N(1′)	−720(8)	2 587(10)	−1 320(16)
C(1′)	−101(8)	2 841(9)	−1 311(14)
C(2′)	396(10)	2 454(13)	−969(14)
C(3′)	265(10)	1 787(11)	−686(16)
C(4′)	−394(11)	1 476(11)	−770(14)
C(5′)	−855(11)	1 932(13)	−1 111(18)
C(6′)	−58(11)	3 565(11)	−1 606(15)
C(7′)	812(10)	1 320(9)	−249(13)
C(8′)	−523(10)	737(10)	−471(17)
O(1′)	991(7)	2 698(7)	−1 077(11)
O(2′)	−275(10)	280(9)	−1 111(14)
N(2′)	1 359(8)	1 541(8)	−3(15)
C(9′)	1 788(9)	1 066(9)	549(14)
C(10′)	2 288(9)	1 495(10)	1 123(14)
O(3′)	2 304(8)	2 128(8)	1 023(12)
O(4′)	2 660(9)	1 155(8)	1 677(14)
O(W1)	2 500(0)	0(0)	2 730(18)
O(W2)	3 121(8)	3 200(8)	1 733(12)
O(W3)	3 965(9)	4 906(10)	2 369(15)
O(W4)	260(8)	1 859(9)	1 763(13)
O(W5)[c]	1 208(19)	4 733(20)	−2 895(29)
O(W51)[c]	4 356(44)	4 844(46)	−2 606(66)
O(W6)	1 737(18)	1 522(15)	2 516(32)

[a] Occupancy 0.65. [b] Occupancy 0.35. [c] Occupancy 0.5.

being characterized by a bend across the line N(2) ··· O(1) to give a 'sofa' conformation to the ring. The Cu$^{\mathrm{II}}$ ion deviates by 0.15 Å from the mean plane containing the other five atoms. The five-membered ring (III) shows a half-chair distortion with atoms N(2) and C(9) being out of the plane containing the atoms C(10), O(3), and Cu. However, when all the atoms of the individual rings are considered, the deviations are in the range 0.003—0.074 Å for the six-membered ring and 0.001—0.056 Å for the five-membered ring. The dihedral angles between the planes of the rings I and II, II and III, and I and III are 6.3, 6.6, and 1.3°, respectively, indicating that the ligand as a whole deviates from planarity to attain a chair-like conformation.

The bond lengths and angles of the ligand part are in the range observed for similar pyridoxylideneamino acid complexes.^{5a,5b,8} The pyridine nitrogen is protonated [bond angle C(1)–N(1)–C(5) = 124°; the mean non-protonated and protonated bond angles are reported to be 115.7 and 125.0° respectively^{13}] necessitating the phosphate moiety to bear a negative charge to meet the charge neutralization requirement. The phosphate group has two long P–O bonds and two short bonds. With O(6) protonated, the negative charge is shared by the two short bonds.

In the structure, centrosymmetrically related (about 0,0,0) chains of molecules running in zigzag fashion are interleaved into each other. They are interlinked by hydrogen bonds involving phosphate oxygens O(5) and O(6) and co-ordinated oxygens O(3) and O(W1), which form a loose six-membered ring. Such successive pairs are interlinked by another loose eight-membered ring involving hydrogen bonding between phosphate oxygens O(5) and O(7) and their centrosymmetrically related equivalents *via* water molecules O(W2) and O(W2)$^{\mathrm{II}(110)}$ (Table 6, Figure 3). The chains along the *c* direction also are interlinked by a loose four-membered ring involving O(4), O(W4), and their symmetry related (about $0,0,\frac{1}{2}$) equivalents. The interactions between N(1) and O(7)$^{\mathrm{III}(011)}$ and among the lattice water molecules are the other possible hydrogen bonds present in the structure. Thus in the absence of stacking interactions between two pyridine rings, the

Table 5. Bond lengths (Å) and angles (°) in compound (**2**) with e.s.d.s in parentheses. The second set of values are for the ligand with primed labels

Ni–O(1)	2.01(2)	2.05(2)	O(1)–Ni–O(1′)	93.6(6)		C(4)–C(3)–C(7)	114(4)	116(2)
Ni–N(2)	2.04(2)	1.98(2)	N(2)–Ni–N(2′)	174.0(7)		C(3)–C(4)–C(5)	119(2)	112(2)
Ni–O(3)	2.07(2)	2.07(2)	O(3)–Ni–O(3′)	88.8(6)		C(3)–C(4)–C(8)	125(2)	122(2)
N(1)–C(1)	1.42(3)	1.35(2)	O(1)–Ni–N(2)	91.0(7)	88.0(7)	C(5)–C(4)–C(8)	115(2)	126(2)
N(1)–C(5)	1.32(3)	1.33(3)	O(1)–Ni–O(3)	169.9(6)	169.3(6)	N(1)–C(5)–C(4)	122(2)	124(2)
C(1)–C(2)	1.47(3)	1.34(3)	O(1)–Ni–O(3′)	88.8(6)	90.6(6)	C(3)–C(7)–N(2)	121(3)	123(2)
C(1)–C(6)	1.53(4)	1.47(3)	O(1)–Ni–N(2′)	93.3(7)	96.0(7)	C(4)–C(8)–O(2)	112(3)	112(2)
C(2)–C(3)	1.41(3)	1.38(3)	N(2)–Ni–O(3)	79.3(7)	81.5(7)	C(4)–C(8)–O(21)	124(3)	
C(2)–O(1)	1.25(3)	1.30(3)	O(3)–Ni–N(2′)	96.1(7)	94.4(7)	O(2)–C(8)–O(21)	91(4)	
C(3)–C(4)	1.43(4)	1.47(3)	C(1)–N(1)–C(5)	123(2)	123(2)	Ni–O(1)–C(2)	120(1)	119(1)
C(3)–C(7)	1.50(4)	1.56(3)			120(2)	Ni–N(2)–C(7)	128(2)	128(2)
C(4)–C(5)	1.33(4)	1.37(3)	N(1)–C(1)–C(2)	119(2)	114(2)	Ni–N(2)–C(9)	109(2)	114(1)
C(4)–C(8)	1.48(4)	1.52(3)	N(1)–C(1)–C(6)	118(2)	126(2)	C(7)–N(2)–C(9)	122(2)	117(2)
C(7)–N(2)	1.25(3)	1.24(3)	C(2)–C(1)–C(6)	124(2)	119(2)	N(2)–C(9)–C(10)	102(2)	109(2)
C(8)–O(2)	1.44(4)	1.36(3)	C(1)–C(2)–C(3)	114(2)	117(2)	C(9)–C(10)–O(3)	120(2)	120(2)
C(8)–O(21)	1.38(5)		C(1)–C(2)–O(1)	114(2)	123(2)	C(9)–C(10)–O(4)	118(2)	115(2)
N(2)–C(9)	1.51(4)	1.48(3)	C(3)–C(2)–O(1)	131(2)	126(2)	O(3)–C(10)–O(4)	121(2)	125(2)
C(9)–C(10)	1.53(4)	1.54(3)	C(2)–C(3)–C(4)	123(2)	122(2)	Ni–O(3)–C(10)	113(2)	114(1)
C(10)–O(3)	1.28(3)	1.24(3)	C(2)–C(3)–C(7)	123(2)				
C(10)–O(4)	1.30(3)	1.27(3)						

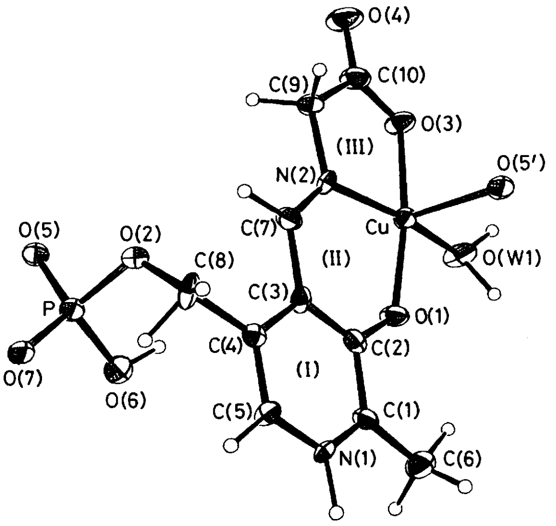

Figure 1. Molecular structure of compound (**1**). Primed atoms are related to the respective unprimed atoms by unit translations along *a*

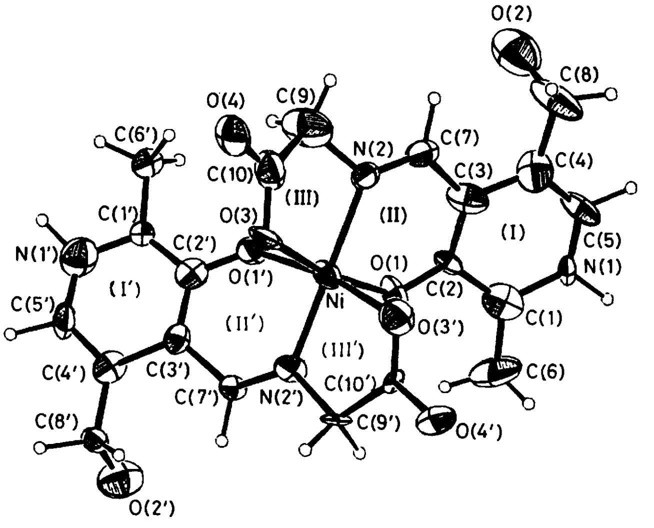

Figure 2. Molecular structure of compound (**2**). For clarity, atom O(21) is not shown

main features governing the packing are the different hydrogen-bonded rings.

Compound (**2**).—In [Ni(Pxd-Gly)$_2$]·6H$_2$O, the Ni^{II} ion is bonded to two tridentate Schiff-base ligands providing a distorted-octahedral environment around the metal ion. The ligands with co-ordination sites phenolic oxygen, imine nitrogen and carboxylate oxygen chelate to the metal ion on octahedral edges, as a result of which the two imine nitrogens are *trans* and carboxylate oxygens and phenolic oxygens are *cis* to each other. The two ligands (unprimed and primed moieties in Figure 2) which are disposed approximately normal to each other are related by a pseudo-two-fold axis passing through the nickel atom. This axis bisects the O(1)–Ni–O(1′) and O(3)–Ni–O(3′) angles and it is nearly parallel to the crystallographic *c* axis. The co-ordinated bond distances are in the range 1.98—2.07 Å. The *cis* bond angles around the central Ni^{II} ion range from 79.3 to 96.1° and the *trans* angles are 169.9, 169.3, and 174.0°.

The bond lengths and angles in the Schiff-base ligands are comparable to those of the compounds reported earlier.[5a,5b,8] The ligands considerably deviate from planarity and this fact can be illustrated by considering one of the ligands. For example, for the 'unprimed' ligand the heterocyclic ring (I) is nearly planar with deviations ranging between 0.02 and 0.05 Å. However, the six-membered chelate ring (II) shows a marked bend across the line N(2)···O(1) and the plane of best fit through the six atoms shows deviations of 0.005—0.200 Å. The five-membered chelate ring (III) is non-planar, the atom C(9) showing a deviation of 0.48 Å from the least-squares plane passing through the five atoms of the ring. The six-membered and five-membered rings show 'near-sofa' and 'half-chair' conformations as in compound (**1**). The dihedral angles between the planes of the rings (I) and (II), (II) and (III), and (I) and (III) are 21.8, 13.2, and 32.7° respectively. These deviations give a curvature to the whole ligand which assumes a boat-like conformation. A similar situation holds for the other ligand also.

The packing of molecules is governed by hydrogen-bonded links *via* lattice water molecules. Glide-related molecules are stacked in the *c* direction and linked in such a way that they

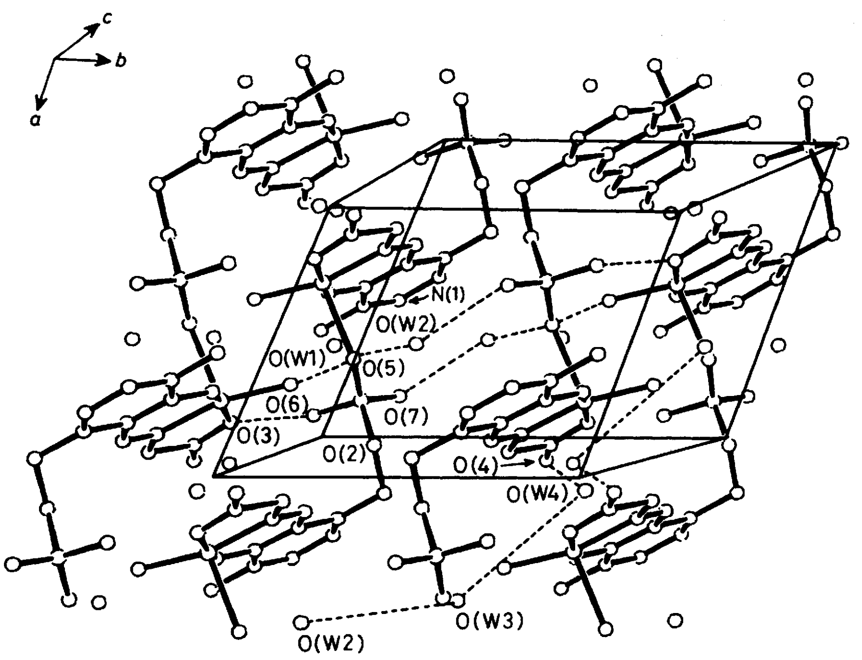

Figure 3. Packing diagram of compound (**1**) illustrating a few of the hydrogen bonds

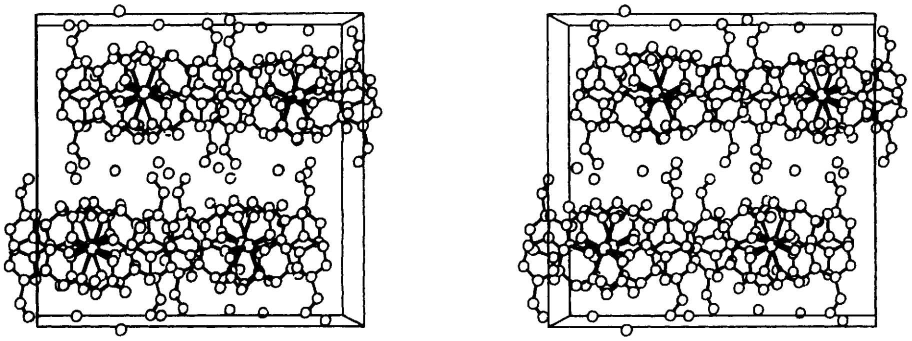

Figure 4. Stereoscopic view of a unit cell of compound (**2**) viewed down *c*

Table 6. Possible hydrogen bonds in compound (**1**)[a]

Donor (D)	Acceptor (A)	A of molecule[b]	Code no.	Distance D··· A (Å)	Angle subtended at the donor atom (°)
N(1)	O(7)	II(011)	1	2.72	C(1)–N(1) ··· 1 = 117.7 C(5)–N(1) ··· 1 = 118.5
O(6)	O(3)	II(000)	2	2.79	P–O(6) ··· 2 = 114.8
O(W1)	O(W3)	I(000)	3	2.67	Cu–O(W1) ··· 3 = 126.0
O(W1)	O(5)	II(000)	4	2.71	Cu–O(W1) ··· 4 = 127.1 3 ··· O(W1) ··· 4 = 102.8
O(W2)	O(5)	I(100)	5	2.87	
O(W2)	O(7)	II(010)	6	2.91	5 ··· O(W2) ··· 6 = 129.0
O(W3)	O(W2)	II(100)	7	2.86	
O(W3)	O(W4)	I(000)	8	2.92	7 ··· O(W3) ··· 8 = 119.1
O(W4)	O(4)	I(001)	9	2.67	
O(W4)	O(4)	II(000)	10	3.10	9 ··· O(W4) ··· 10 = 83.6

[a] Symmetry codes: I *x*, *y*, *z*; II −*x*, −*y*, −*z*. [b] Donor atom always has symmetry code I(000). Acceptor atom belongs to specified symmetry-related molecule with the translations along the three edges of the unit cell as indicated in parentheses.

Table 7. Possible hydrogen bonds in compound (**2**)[a]

Donor (D)	Acceptor (A)	A of molecule[b]	Code no.	Distance D···A(Å)	Angle subtended at the donor atom (°)
N(1)	O(W4)	III(000)	1	2.72	C(1)–N(1)···1 = 122.0
					C(5)–N(1)···1 = 115.0
N(1′)	O(W2)	III($\bar{1}$00)	2	2.69	C(1′)–N(1′)···2 = 130.6
					C(5′)–N(1′)···2 = 106.9
O(2)	O(W5)	II(010)	3	2.77	C(8)–O(2)···3 = 133.0
O(2′)	O(W3)	V($\bar{1}$0$\bar{1}$)	4	2.65	C(8′)–O(2′)···4 = 113.8
O(W1)	O(4′)	I(000)	5	2.70	
O(W2)	O(3′)	I(000)	6	2.84	
O(W2)	O(4′)	IV(000)	7	2.71	6···O(W2)···7 = 115.1
O(W3)	O(4)	II(010)	8	2.65	
O(W3)	O(W1)	IV(000)	9	2.97	8···O(W3)···9 = 99.5
O(W4)	O(3)	I(000)	10	2.77	10···O(W4)···11 = 117.5
O(W4)	O(4)	IV(000)	11	2.72	12···O(W6)···11 = 51.2
O(W6)	O(3)	IV(000)	12	2.73	12···O(W6)···6 = 128.2
O(W6)	O(4)	IV(000)	11	2.44	12···O(W6)···5 = 156.0
O(W6)	O(3′)	I(000)	6	2.65	11···O(W6)···6 = 148.2
O(W6)	O(4′)	I(000)	5	2.32	11···O(W6)···5 = 144.2

[a] Symmetry codes: I x, y, z; II $\frac{1}{2} - x, -y, z$; III $\frac{1}{2} + x, y, -z$; IV $x, \frac{1}{2} - y, \frac{1}{2} - z$; V $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$. [b] Donor atom always has symmetry code I(000). Acceptor atom belongs to specified symmetry related molecule with the translations along the three edges of the unit cell as indicated in parentheses.

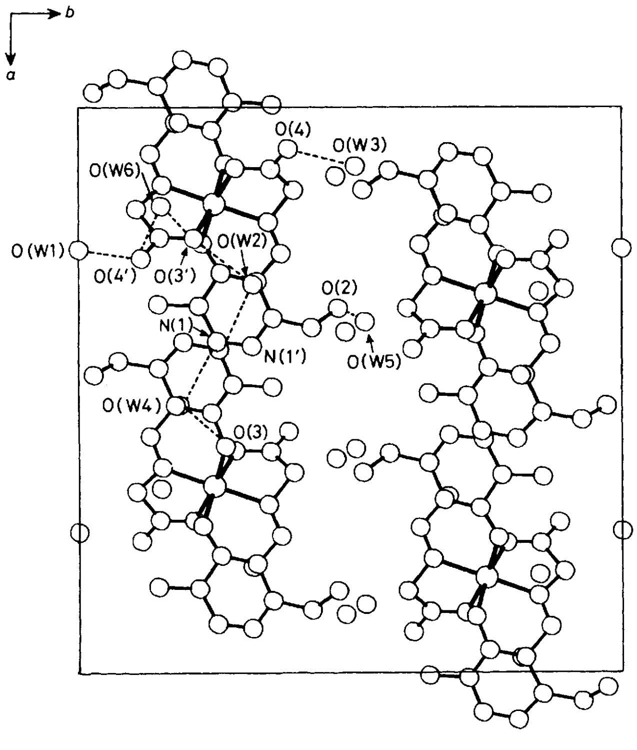

Figure 5. Packing diagram of compound (**2**) showing some hydrogen bonds. For clarity, only four molecules are shown. Alternative positions of O(2) and O(W5) are not shown

form a sheet-like structure in the (010) plane (Figure 4). The pyridine nitrogen atoms of both the ligands are protonated [C(1)–N(1)–C(5) 123, C(1′)–N(1′)–C(5′) = 123°]. These nitrogens and co-ordinated carboxylate oxygens O(3) and O(3′), which are in interior parts of the sheet, are hydrogen-bonded to water molecules O(W2), O(W4), and O(W6) lying between the stacks along *c* (Table 7, Figure 5). The protruding groups O(2), O(2′), O(4), and O(4′) are similarly hydrogen-bonded to the water molecules O(W1), O(W3), and O(W5), which lie in the vacant space between the sheets (Figure 5). A peculiar feature with O(W6) is that it is at a distance of 2.32—2.73 Å from the four carboxylate oxygens [O(3) and O(4) of one molecule and O(3′) and O(4′) of another] (Table 7). It may be that each of the protons of O(W6) is involved in bifurcated hydrogen bonding with the two oxygens of a carboxylate group or alternatively, O(W6) tumbles around continuously to have partial hydrogen bonds with all of these oxygen atoms. The high thermal parameter (U = 0.2196 Å^2) for this atom supports this view. Much significance need not be attached to the unusually short O(4)···O(W6) (2.44 Å) and O(4′)···O(W6) (2.32 Å) distances which may be due to disorder of the water molecule and inaccuracy associated with its positional parameters. Further, O(W5), which is involved in only one hydrogen bond with O(2), is virtually hanging loose in the lattice. In fact, alternative positions for these two atoms have been observed [O(21) and O(W51)] and these are in turn linked by a hydrogen bond.

Discussion

While the structure of (**1**) is refined to a good degree of accuracy, that of (**2**) can only be considered satisfactory. The main cause for this is probably the poor crystal quality of the latter compound; crystals are unevenly shaped, abruptly truncated, semi-transparent solid blocks. Such a situation has been encountered by earlier workers and the poor quality of the crystals has been ascribed to an incomplete racemization before crystallization[5a] or to internal disorder of the water molecules,[5c,6–8] which are present in quantity in the crystals. Compound (**1**) has three lattice water molecules which are relatively well fixed in the lattice through hydrogen bonds, whereas in (**2**) two of the six waters are disordered (high thermal parameters and alternative positions). Further, the glycine moiety which is present in both the complexes does not have any asymmetric centre. Thus the major contribution to the poor quality of the crystals is from internal disorder of water molecules.

The standard deviations in bond lengths and angles are considerably large for both the structures, making the manifestation of electronic changes through the π-cloud inconclusive. This drawback is common to all published structures of pyridoxylideneamino acid complexes.[5–8] However, reasonable structure–activity relationships have been conceived either on the basis of useful comparisons between appropriate complexes and the uncomplexed compounds or by comparing structures of different complexes. For example, in (pyridoxylidenevalinato)copper(II),[7] shortening of C(1)–C(2), C(4)–C(5), and C(3)–C(7) and lengthening of C(7)–N(2) and C(3)–C(4) bonds by considerable extents has been observed when compared to those of pyridoxime phosphate[14] or pyridoxamine phosphate hydrochloride.[15] This has been attributed, to some extent, to the pyridoxal moiety being locked into the quinonoid form formally postulated as occurring during the reaction sequence. The lengthening of the C(9)–C(10) bond further favours this kind of electron distribution. However, in (**1**) and (**2**) such distinct deviations in bond lengths have not been observed and bond lengths more appropriately resemble those of bis(pyridoxylidenevalinato)nickel(II), [Ni(Pxd-Val)$_2$],[8] and bis(pyridoxylidenevalinato)manganese(II)[5a] complexes. The C(2)–O(1) distances in both (**1**) and (**2**) are shorter than those in other pyridoxylideneamino acid complexes, an indication of more double-bond character in this bond. A few bond lengths in the two ligands in (**2**) differ slightly from each other (Table 5). This may be due to electron redistribution in the ligands to different extents.

Striking similarities between the structures of (**1**) and aqua[(5′-phosphopyridoxylidene)phenylalaninato]copper(II), [Cu(*P*-Pxd-Phe)(H_2O)];[6] and between (**2**) and [Ni(Pxd-Val)$_2$],[8] are particularly noteworthy. In both (**1**) and [Cu(*P*-Pxd-Phe)(H_2O)], the Cu^{II} ion is in a square-pyramidal environment bonded to the same kind of donors. The pyridine nitrogen is protonated and the phosphate moiety bears a negative charge to satisfy electrical neutrality. Of the two short P–O bonds one is bonded to Cu^{II} at the axial site and the other is involved in hydrogen bonding with the pyridinium ion. Similarly, (**2**) and [Ni(Pxd-Val)$_2$] have approximate octahedral environments around the Ni^{II} ions due to the co-ordination of two tridentate Schiff-base ligands which are related by a pseudo-two-fold axis. However, in [Ni(Pxd-Val)$_2$] the hydroxymethyl groups of the two ligands have different conformations, but in (**2**) the conformations are the same [when O(2) with the higher occupancy factor is considered]. Both the structures consist of Δ and Λ conformers as a consequence of the centrosymmetric space groups. In both the complexes, each of the ligands remarkably deviates from planarity when compared to the copper complexes. This may be due to the larger co-ordination distances in nickel complexes than in copper complexes, which result in a puckering of the chelated Schiff bases.[8]

The planarity of the pyridoxylidene Schiff bases has always been considered to be important in explaining the reactivities of metal–pyridoxylideneamino acid systems,[8] since it is believed that it is this planarity of the ligand which allows the facile electron transfer through the extended conjugated system for the reaction to occur. In (salicylideneglycinato)copper(II),[16] a compound analogous to (**1**), the three rings are almost planar. However, in (**1**) the rings are less planar and ring planes (I) and (II) form a dihedral angle of 6.3° (see Table 5 of SUP 56251). Furthermore the ring plane (III) makes angles of 6.6 and 1.3° with the ring planes (II) and (I) respectively. However, for (**2**), these values are as high as 21.8, 13.2, and 32.7° for the unprimed ligand and 19.7, 13.7, and 31.8° for the primed ligand (Table 6 of SUP 56251). This difference, namely the near planarity of the copper chelate and the considerable non-planarity of the nickel chelate, may explain the observed higher and lower activities of Cu^{II} and Ni^{II} ions in the non-enzymatic reactions.[9] Another aspect, generally considered in explaining the reactivity, is the relative orientation of the α-C–H bond with respect to the aldimine (*i.e.*, –CH=N–CH$_2$–) plane.[7,17,18] The α-C–H bond breaking is the key step in racemization, transamination, and β-elimination reactions and according to Dunathan's hypothesis[19] the bond to be cleaved must be perpendicular to the plane of the extended π-system to optimize σ–π overlap. However, in our systems, as glycine is the amino acid used, there are two α-C–H bonds and so definite conclusions cannot be drawn in this regard. While both the bonds make angles close to 90° with the aldimine plane {torsion angles: C(7)–N(2)–C(9)–H(1)[C(9)] = 62.0° and C(7)–N(2)–C(9)–H(2)[C(9)] = −55.1°} in (**1**), in (**2**) one of the hydrogens lies close to the aldimine plane {C(7)–N(2)–C(9)–H(2)[C(9)] = −32.1° and C(7′)–N(2′)–C(9′)–H(2′)[C(9′)] = −42.7°} while the other hydrogen is nearly perpendicular to the plane {C(7)–N(2)–C(9)–H(1)[C(9)] = 96.9° and C(7′)–N(2′)–C(9′)–H(1′)[C(9′)] = 80.1°}. Hence systems with Schiff bases derived from higher amino acids may be more helpful in deriving definite conclusions regarding the reactivity on the basis of the orientations of the bonds at the α-carbon atom.

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