Ternary Metal Complexes of Vitamin B_6 Related Compounds. Crystal and Molecular Structures of Copper(II)–2,2′-Bipyridyl-Pyridoxic Acid and Copper(II)–2,2′-Bipyridyl–Pyridoxic Acid γ-Lactone Complexes†

S. P. Sudhakara Rao and Hattikudur Manohar*
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India
Katsuyuki Aoki* and Hiroshi Yamazaki
The Institute of Physical and Chemical Research, Wako-Shi, Saitama 351, Japan

Attempts to prepare ternary metal complexes of pyridoxylidene Schiff bases resulted in the novel oxidation of pyridoxal to pyridoxic acid (Hpa) or its γ-lactone (pal). The *X*-ray structures of three ternary metal complexes of the oxidised products are reported. The complexes, characterized also by i.r. spectroscopy, are [Cu(bipy)(pa)Cl]·$2H_2O$ (**1**) (bipy = 2,2′-bipyridyl), [Cu(bipy)(pa)(ClO_4)] (**2**), and [Cu(bipy)(pal)(NO_3)]NO_3 (**3**). Crystals of (**1**) are monoclinic, space group $P2_1/n$, a = 14.342(2), b = 8.374(1), c = 17.331(2) Å, β = 112.31(1)°, and Z = 4; crystals of (**2**) are monoclinic, space group $P2_1/c$, a = 9.782(3), b = 14.440(4), c = 14.541(3) Å, β = 103.58(2)°, and Z = 4; crystals of (**3**) are triclinic, space group $P\bar{1}$, a = 8.388(2), b = 8.724(1), c = 15.483(2) Å, α = 99.37(1), β = 76.82(2), γ = 117.05(1)°, and Z = 2. The structures were solved by the heavy-atom method and refined to R values of 0.046, 0.039, and 0.049 for 3 030, 1 642, and 3 054 independent diffractometer data respectively. The co-ordination geometry around the metal ion is distorted square pyramidal in (**1**) and (**3**) and tetragonally elongated (4 + 1 + 1) octahedral in (**2**). Two oxygens from phenolic and carboxylate or carbonyl groups of pa or pal and two nitrogens from bipy form the base, while the axial site is occupied by a chloride ion in (**1**), perchlorate oxygen in (**2**), or a nitrate oxygen in (**3**). In (**2**), phenolic oxygen, which acts as the other axial site, bridges two Cu^{II} centres resulting in a dimer. Both pa and pal are zwitterionic and the protonated pyridine nitrogens are involved in hydrogen bonding. Partial stacking between the pyridine ring and one of the bipy rings is observed in (**2**) and (**3**).

Despite the importance of the metal complexes of the B_6 vitamins and of their Schiff bases,[1–4] interactions of B_6 vitamins or related compounds with metals in ternary systems have been little studied. Our recent report on ternary complexes of pyridoxine (Hpn) with Co^{III} and Cu^{II} is the first crystallographic work on such systems.[5] Apart from the complexes of this type, ternary metal complexes of pyridoxylidene amino-acid Schiff bases are of further interest in view of the fact that the decarboxylation reaction, which is not favoured in a binary system involving a tridentate Schiff-base complex, is favoured in a ternary system of a bidentate Schiff-base complex.[6] The latter observation is well explained in terms of Dunathan's hypothesis[7] which states that in pyridoxylidene amino-acid Schiff bases, the bond on the α-carbon atom perpendicular to the extended π-system is most amenable for cleavage. As far as we are aware, no work has been done in the solid state to support this suggestion of Martell.[6]

In order to study the stereochemistry around the α-carbon atom and to draw the possible structure–activity relationships, we have initiated a programme of preparing ternary pyridoxylidene amino-acid Schiff-base complexes and characterizing them mainly by *X*-ray techniques. However, our initial attempts in this direction led to some unexpected results which have been reported in brief.[8] The complexes obtained were of the oxidised products of pyridoxal (Hpl) instead of the intended pyridoxylidene amino-acid Schiff bases. This paper details the preparation, spectroscopic characterization, and *X*-ray structural studies of three complexes: (2,2′-bipyridyl)chloro(pyridoxato)copper(II) dihydrate, [Cu(bipy)(pa)Cl]·$2H_2O$ (**1**); (2,2′-bipyridyl)perchlorato(pyridoxato)copper(II), [Cu(bipy)(pa)(ClO_4)] (**2**); and (2,2′-bipyridyl)nitrato(pyridoxic acid γ-lactone)copper(II) nitrate, [Cu(bipy)(pal)(NO_3)]NO_3 (**3**). Little is known concerning the oxidation of Hpl and the structures reported in this paper are the first *X*-ray structural results on complexes containing pa and pal.

Experimental

Preparations.—Compound (**1**). The compound was obtained from a 1:1:1:1 mixture of $Cu(NO_3)_2·3H_2O$, Hpl·HCl, bipy and L-histidine in water (pH *ca.* 3.0). It was also obtained from a 1:1:1:1 mixture of $Cu(ClO_4)_2·6H_2O$, Hpl, bipy and DL-alanine (pH *ca.* 4.0). The deep green plate-like crystals obtained after *ca.* 1 week were filtered off and air dried. The chloride ion in the compound obtained from the latter preparation may have come from the dissociation of the perchlorate group.[5]

Compound (**2**). Bluish-green parallelopiped-shaped crystals of (**2**) separated out from a solution of a 1:1:1:1 mixture of $Cu(ClO_4)_2·6H_2O$, Hpl, bipy and glycine in water–ethanol (1:1) (pH *ca.* 4.0).

Compound (**3**). A 1:1:1:1 mixture of $Cu(NO_3)_2·3H_2O$, bipy, Hpl, and DL-alanine was dissolved in water–ethanol (1:1) and a bluish green solution was obtained (pH *ca.* 3.9). After 2 d,

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Abbreviations: Hpn = pyridoxine (5-hydroxy-6-methylpyridine-3,4-dimethanol), Hpa = 4-pyridoxic acid (3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carboxylic acid), pal = pyridoxic acid γ-lactone {7-hydroxy-6-methylfuro[3,4-*c*]pyridin-3(1*H*)-one}, Hpl = pyridoxal (3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carbaldehyde), and Hpm = pyridoxamine (4-aminomethyl-5-hydroxy-6-methylpyridine-3-methanol).

Non-S.I. unit employed: B.M. ≈ 9.274×10^{-24} J T^{-1}.

Table 1. Summary of crystal data collection and structure refinement

Compound	**(1)**	**(2)**	**(3)**
Formula	$C_{18}H_{20}ClCuN_3O_6$	$C_{18}H_{16}ClCuN_3O_8$	$C_{18}H_{15}CuN_5O_9$
M	473.4	501.3	508.9
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	14.342(2)	9.782(3)	8.388(2)
b/Å	8.374(1)	14.440(4)	8.724(1)
c/Å	17.331(2)	14.541(3)	15.483(2)
α/°	90	90	99.37(1)
β/°	112.31(1)	103.58(2)	76.82(2)
γ/°	90	90	117.05(1)
U/Å^3	1 925.7	1 996.5	980.2
Z	4	4	2
D_m/Mg m$^{-3\,a}$	1.62	1.61	1.72
D_c/Mg m^{-3}	1.63	1.66	1.72
F(000)	972	1 020	518
Diffractometer	Rigaku	Syntex $P2_1$	Rigaku
Radiation (λ/Å)	Mo-K_α (0.7107)	Mo-K_α (0.7107)	Mo-K_α (0.7107)
T/K	298	296	298
Reflections measured	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, \pm k, \pm l$
Scan type	ω for $2\theta \leqslant 30°$ ω–2θ for $2\theta > 30°$	ω–2θ	ω for $2\theta \leqslant 30°$ ω–2θ for $2\theta > 30°$
Scan speed (° min^{-1})	4.0	2.5—12.5	4.0
θ Range (°)	1.5—27.5	1.5—22.5	2—27.5
Crystal size (mm)	0.34 × 0.31 × 0.09	0.20 × 0.18 × 0.12	0.30 × 0.12 × 0.08
No. of reflections measured	4 430	2 598	3 595
No. of observed unique reflections	3 030 [$F > 3\sigma(F)$]	1 642 [$I > 3\sigma(I)$]	3 054 [$F > 5\sigma(F)$]
μ(Mo-K_α)/cm^{-1}	13.08	12.75	11.80
Transmission factors^b	0.84—1.07	0.95—1.05	0.91—1.06
Weighting scheme (w)	$[\sigma^2(F)]^{-1}$	$[\sigma^2(F) + 0.002\,F^2]^{-1}$	$[\sigma^2(F) + 0.0063\,F^2]^{-1}$
R^c	0.046	0.039	0.049
R'^d	0.050	0.045	0.078
Largest peak in final difference map (e Å^{-3})	0.56	0.24	0.24

[a] By flotation in $CHCl_3$–$CHBr_3$. [b] Normalized to an average of unity. [c] $R = \Sigma|F_o - |F_c||/\Sigma F_o$. [d] $R' = [\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$.

acicular green crystals of (3) crystallized out of the solution. These were filtered off and dried under vacuum.

Physical Measurements.—The i.r. spectra for the compounds (KBr matrix) were recorded on a Perkin-Elmer 599 spectrophotometer. The room-temperature magnetic susceptibilities were measured by the Faraday method using $Hg[Co(CNS)_4]$ as calibrant.

X-Ray Data Collection and Reduction.—Oscillation and Weissenberg photographs were employed to determine the preliminary crystal data. The unit-cell dimensions and their associated standard deviations were derived from a least-squares fit to the setting angles of *ca.* 20 high-angle reflections measured on automated diffractometers. Details of the data collection and processing are presented in Table 1. The data were corrected for Lorentz and polarization effects and those of (2) for absorption effects as well.[9]

Solution and Refinement of the Structures.—For all the compounds, the structure solution was straightforward and was carried out by the conventional heavy-atom method. All the hydrogen atoms were located from difference electron-density maps and included in the structure factor calculations with their parameters being refined in the last few cycles. Full-matrix least squares was employed for structure refinement with the term $\Sigma(F_o - |F_c|)^2$ being minimized. The final difference electron-density maps were essentially featureless. Programs and the scattering factors used for the calculations were as given in an earlier paper.[5] The final atomic co-ordinates are given in Table 2, selected bond distances and angles are given in Table 3.

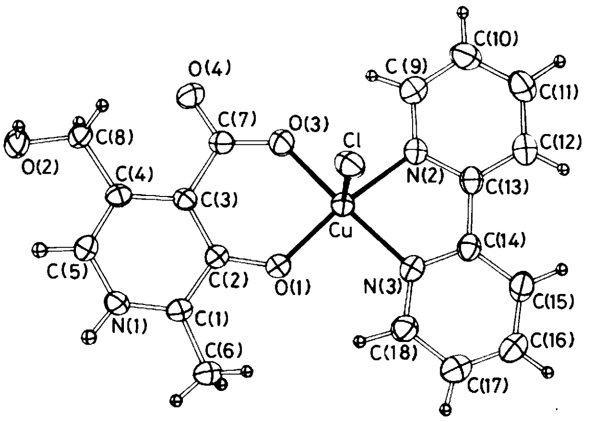

Figure 1. Molecular structure of (1). Hydrogens are included but not labelled; water molecules are omitted

Results and Discussion

Infrared Spectra.—The i.r. spectra of the compounds showed some characteristic peaks. The absence of a band at *ca.* 1 630 cm^{-1} corresponding to an azomethine stretch[10] in the spectra of (1) and (2) indicates that no Schiff base is formed. However, a peak of medium intensity at *ca.* 1 505 cm^{-1}, which can be ascribed to phenolic C–O$^-$ bond stretching,[5,11] indicates the possible presence of the Hpl ligand. The presence of the co-ordinated bipy group in the compounds is unambiguously

Table 2. Fractional atomic co-ordinates (× 10^4) for non-hydrogen atoms in compounds (**1**)—(**3**), with estimated standard deviations (e.s.d.s) in parentheses

	(**1**)			(**2**)			(**3**)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Cu	1 321.5(4)	855.2(7)	−531.9(3)	1 194(1)	4 141(1)	5 624(1)	383(1)	848(1)	2 356(0)
N(1)	−1 173(2)	4 149(4)	384(2)	−1 092(7)	3 134(4)	2 159(4)	4 069(5)	7 567(4)	2 766(2)
C(1)	−276(3)	3 467(5)	572(2)	−241(7)	3 676(5)	2 760(4)	3 485(6)	6 048(5)	3 114(3)
C(2)	−111(3)	2 470(5)	−30(2)	−196(6)	3 594(5)	3 751(4)	2 307(5)	4 521(5)	2 677(3)
C(3)	−943(3)	2 137(5)	−777(2)	−970(7)	2 869(5)	4 038(4)	1 853(5)	4 790(5)	1 927(2)
C(4)	−1 873(3)	2 918(5)	−936(2)	−1 867(7)	2 322(5)	3 349(4)	2 450(6)	6 386(5)	1 607(3)
C(5)	−1 960(3)	3 932(5)	−345(3)	−1 915(8)	2 502(5)	2 412(5)	3 622(6)	7 823(5)	2 040(3)
C(6)	527(3)	3 767(6)	1 406(3)	702(9)	4 336(6)	2 413(5)	4 055(7)	5 998(6)	3 950(3)
C(7)	−840(3)	975(5)	−1 408(2)	−826(7)	2 678(5)	5 085(4)	664(6)	3 498(5)	1 364(3)
C(8)	−2 799(3)	2 737(6)	−1 740(3)	−2 806(10)	1 561(7)	3 568(5)	1 654(6)	6 145(5)	799(3)
O(1)	802(2)	1 948(4)	174(2)	581(5)	4 213(3)	4 290(3)	1 747(4)	3 033(4)	2 974(2)
O(2)	−3 563(2)	3 861(4)	−1 787(2)	−3 619(8)	1 144(6)	2 711(4)	515(4)	4 263(4)	718(2)
O(3)	0(2)	418(4)	−1 329(2)	−222(5)	3 255(3)	5 706(3)	−146(5)	1 878(4)	1 460(2)
O(4)	−1 620(2)	592(5)	−2 004(2)	−1 343(6)	1 947(4)	5 294(3)	2 967(5)^a	744(5)^a	1 358(2)^a
N(2)	1 954(2)	−701(4)	−1 058(2)	1 931(6)	4 213(4)	7 022(4)	−1 263(4)	−1 627(4)	2039(2)
C(9)	1 511(3)	−1 354(6)	−1 821(3)	1 465(8)	3 734(6)	7 670(5)	−2 194(6)	−2 247(6)	1 359(3)
C(10)	2 055(4)	−2 388(7)	−2 148(3)	2 034(9)	3 824(7)	8 624(5)	−3 260(6)	−3 989(6)	1 190(3)
C(11)	2 992(4)	−2 795(7)	−1 675(3)	3 129(10)	4 425(7)	8 906(5)	−3 375(6)	−5 135(5)	1 743(3)
C(12)	3 452(3)	−2 123(6)	−890(3)	3 632(9)	4 903(6)	8 253(5)	−2 421(6)	−4 527(5)	2 431(3)
C(13)	2 925(3)	−1 069(5)	−604(3)	3 017(7)	4 801(5)	7 298(5)	−1 390(5)	−2 770(5)	2 570(3)
C(14)	3 351(3)	−228(5)	211(3)	3 475(7)	5 273(5)	6 517(5)	−324(6)	−2 001(5)	3 296(3)
C(15)	4 345(3)	−401(6)	773(3)	4 605(8)	5 877(6)	6 650(5)	−344(7)	−2 949(6)	3 941(3)
C(16)	4 662(3)	508(6)	1 497(3)	4 935(9)	6 282(6)	5 883(6)	809(8)	−2 099(7)	4 575(3)
C(17)	4 008(4)	1 513(6)	1 649(3)	4 126(8)	6 087(5)	4 991(6)	1 914(7)	−364(7)	4 522(3)
C(18)	3 022(3)	1 634(6)	1 076(3)	3 027(8)	5 473(5)	4 909(5)	1 848(7)	502(6)	3 869(3)
N(3)	2 712(2)	758(5)	367(2)	2 703(6)	5 068(4)	5 652(4)	747(5)	−291(4)	3 272(2)
Cl	1 610.9(9)	3 251(1)	−1 422.7(7)	3 596(2)	2 221(2)	6 079(2)			
O(5)	4 825(3)^b	5 024(6)^b	1 034(3)^b	2 855(6)^c	2 866(4)^c	5 398(4)^c	2 057(8)^a	−335(5)^a	129(4)^a
O(6)	5 996(3)^b	6 814(5)^b	427(3)^b	4 835(7)^c	1 915(5)^c	5 797(6)^c	4 047(7)^a	2 244(6)^a	233(3)^a
O(7)				3 979(11)^c	2 639(6)^c	6 956(5)^c	−4 114(6)^a	1 512(5)^a	2920(3)^a
O(8)				2 813(9)^c	1 429(6)^c	6 101(6)^c	−2 484(9)^a	2 912(5)^a	3 905(3)^a
O(9)							−3 218(6)^a	214(4)^a	3 596(4)^a
N(4)							3 066(5)	875(5)	551(2)
N(5)							−3 268(6)	1 553(5)	3 485(2)

Co-ordinates for ^{a} nitrate, ^{b} water, and ^{c} perchlorate oxygens.

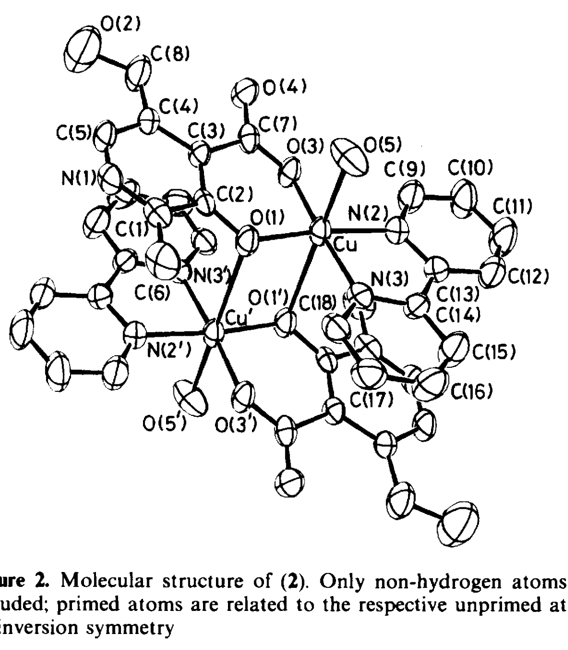

Figure 2. Molecular structure of (**2**). Only non-hydrogen atoms are included; primed atoms are related to the respective unprimed atoms by inversion symmetry

indicated by peaks at 1 600, 1 490, 1 440, and 620 cm^{-1}.[5] The strong bands at *ca.* 1 590 and *ca.* 1 380 cm^{-1} correspond to a co-ordinated carboxylate group.[12] The splitting in the peaks corresponding to the perchlorate group at 1 100 and 620 cm^{-1} in the spectrum of (**2**) can be ascribed to a co-ordinated perchlorate ion.

The spectrum of (**3**) was initially assumed to correspond to a Schiff-base complex due to the presence of a strong peak at 1 665 cm^{-1} and its possible assignment to a azomethine stretch.[12] However, as the structural study revealed the presence of a lactone moiety, the peak is ascribed to this group. Normally γ-lactones should absorb at 1 730—1 750 cm^{-1}. The large difference between this range and the value observed can be explained in terms of two factors: (*i*) the electron-withdrawing effect upon co-ordination of carbonyl oxygen to a metal ion, and (*ii*) possible electron delocalisation to the other C–O bond of the lactone (see below). The presence of the nitrate anion is indicated by a strong broad band at 1 380 cm^{-1}.

X-*Ray Structures*.—The molecular structures and atomic numbering of the three compounds (**1**)—(**3**) are shown in Figures 1—3 respectively and the packing diagrams in Figure 4.

Co-ordination geometry and chelate rings. There is a change in the donor atoms as a result of the conversion of Hpl to pa or pal in the complexes. While phenolic oxygen O(1) is one of the sites as usual,[13] the other is carboxylate oxygen in pa and carbonyl oxygen in pal. Thus both pa and pal form six-membered chelate rings on ligation to the metal. The co-ordination geometry around the metal ion is distorted square pyramidal in (**1**) and (**3**)

Table 3. Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses*

	(1)	**(2)**	**(3)**
Cu–O(1)	1.892(4)	1.893(4)	1.945(3)
Cu–O(3)	1.910(3)	1.910(5)	1.994(4)
Cu–N(2)	1.996(4)	1.994(6)	2.015(3)
Cu–N(3)	2.012(3)	1.985(6)	2.005(4)
Cu–X	2.659(1)	2.528(6)	2.388(4)
Cu–O(1′)		2.964(5)	
N(1)–C(1)	1.330(6)	1.315(9)	1.345(5)
N(1)–C(5)	1.349(5)	1.324(10)	1.343(6)
C(1)–C(2)	1.424(6)	1.435(8)	1.423(6)
C(1)–C(6)	1.488(5)	1.494(11)	1.491(7)
C(2)–C(3)	1.416(5)	1.411(10)	1.386(6)
C(2)–O(1)	1.296(5)	1.308(8)	1.287(5)
C(3)–C(4)	1.416(5)	1.409(9)	1.383(6)
C(3)–C(7)	1.512(6)	1.521(8)	1.442(6)
C(4)–C(5)	1.372(6)	1.378(9)	1.377(6)
C(4)–C(8)	1.524(5)	1.513(12)	1.490(7)
C(7)–O(2)			1.346(6)
C(7)–O(3)	1.250(5)	1.267(8)	1.277(5)
C(7)–O(4)	1.242(4)	1.239(9)	
C(8)–O(2)	1.423(6)	1.443(10)	1.478(5)
O(1)–Cu–O(3)	91.6(6)	92.3(2)	95.5(1)
O(1)–Cu–N(2)	166.0(1)	173.3(2)	165.0(1)
O(1)–Cu–N(3)	92.1(1)	92.3(2)	86.8(1)
O(1)–Cu–X	101.4(1)	88.0(2)	95.4(1)
O(3)–Cu–N(2)	92.5(1)	93.7(2)	96.4(1)
O(3)–Cu–N(3)	166.3(1)	175.4(2)	176.4(2)
O(3)–Cu–X	93.2(1)	91.0(2)	91.5(1)
N(2)–Cu–N(3)	80.7(1)	81.6(2)	80.9(1)
N(2)–Cu–X	91.7(1)	94.6(2)	93.3(1)
N(3)–Cu–X	98.8(1)	89.8(2)	91.0(1)

	(1)	**(2)**	**(3)**
O(1)–Cu–O(1′)		87.2(2)	
O(3)–Cu–O(1′)		95.4(2)	
N(2)–Cu–O(1′)		89.4(2)	
N(3)–Cu–O(1′)		84.2(2)	
X–Cu–O(1′)		172.2(2)	
C(1)–N(1)–C(5)	124.0(4)	123.9(6)	126.6(4)
N(1)–C(1)–C(2)	119.1(4)	118.9(6)	118.6(4)
N(1)–C(1)–C(6)	119.0(4)	120.0(6)	119.8(4)
C(2)–C(1)–C(6)	121.9(4)	121.1(6)	121.6(4)
C(1)–C(2)–C(3)	117.9(4)	117.8(6)	114.6(4)
C(1)–C(2)–O(1)	115.4(4)	114.9(6)	120.8(4)
C(3)–C(2)–O(1)	126.6(4)	127.3(6)	124.6(4)
C(2)–C(3)–C(4)	119.5(4)	119.6(6)	124.7(4)
C(2)–C(3)–C(7)	120.5(4)	120.1(6)	126.9(4)
C(4)–C(3)–C(7)	120.0(4)	120.4(6)	108.4(4)
C(3)–C(4)–C(5)	119.1(4)	117.9(6)	118.6(4)
C(3)–C(4)–C(8)	124.2(4)	124.5(6)	108.8(4)
C(5)–C(4)–C(8)	116.7(4)	117.6(6)	132.6(4)
N(1)–C(5)–C(4)	120.1(4)	121.5(7)	116.8(4)
C(3)–C(7)–O(2)			109.5(4)
C(3)–C(7)–O(3)	121.0(4)	120.8(6)	125.8(4)
C(3)–C(7)–O(4)	117.6(4)	116.9(6)	
O(2)–C(7)–O(3)			124.7(4)
O(3)–C(7)–O(4)	121.4(4)	122.4(6)	
C(4)–C(8)–O(2)	111.8(4)	111.1(7)	103.2(4)
Cu–O(1)–C(2)	126.3(3)	125.2(4)	124.3(3)
C(7)–O(2)–C(8)			110.2(3)
Cu–O(3)–C(7)	131.2(3)	128.3(4)	121.4(3)
Cu–N(2)–C(9)	126.0(3)	126.3(5)	127.7(3)
Cu–N(2)–C(13)	115.5(3)	114.1(5)	114.6(3)
Cu–N(3)–C(14)	115.0(3)	114.9(5)	114.6(3)
Cu–N(3)–C(18)	124.6(3)	126.7(5)	126.1(3)

* X Represents the axial donor atom which is Cl for (**1**), O(5) of perchlorate for (**2**), and O(4) of nitrate for (**3**). O(1′) for (**2**) is related to O(1) by a centre of symmetry at (0, $\frac{1}{2}$, $\frac{1}{2}$).

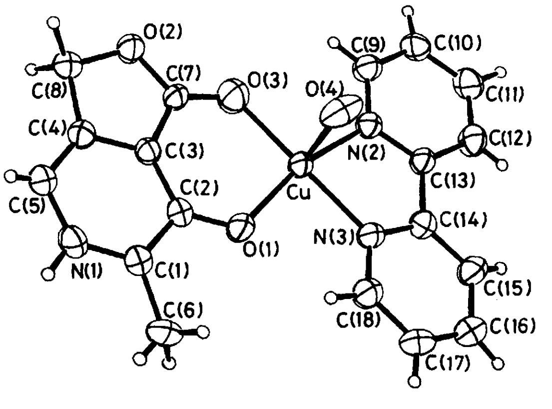

Figure 3. Molecular structure of (**3**). Hydrogen atoms are included as circles; non-co-ordinated atoms of the nitrate groups are omitted

and tetragonally elongated (4 + 1 + 1) octahedral in (**2**). Two sites each from pa or pal and bipy form the base of the square pyramid or octahedron in all cases. The axial site is occupied by chloride ion in (**1**), and a nitrate oxygen O(4) in (**3**). The co-ordination plane is strictly planar in (**1**), but in (**3**) the four atoms forming the basal plane exhibit slight tetrahedral distortions (−0.046 to 0.066 Å). The Cu^{II} ion deviates from this plane by 0.2143(6) and 0.105(1) Å and this plane makes dihedral angles of 7.32 and 6.77° with the pyridine ring in (**1**) and (**3**) respectively.

In (**2**), the co-ordination pattern is interesting due to the bridging nature of O(1). This atom bridges two centrosymmetrically related Cu^{II} centres by being an equatorial donor for one and an axial donor for the other. Thus the molecule is a dimer with a centre of inversion at the centre of the four-membered bridged ring (Figure 2). Such a bridging mode through phenolic oxygen has been observed previously in two other vitamin B_6 complexes, but with some differences. In $[Cd(Hpn)Cl_2]$[14] there are two bridging atoms, O(1) and Cl. This arrangement continues in a chain resulting in a polymeric structure; the Cd–Cd distance is 3.71 Å. Moreover, both the co-ordination bonds of O(1) form part of the equatorial planes of the two metal centres and the two bond lengths are nearly equal (2.307 and 2.317 Å).[14] On the other hand, in (**2**), the metal ions are bridged by two phenolic oxygens with equatorial and axial bond distances of 1.893(4) and 2.964(5) Å respectively. The distance between the two Cu^{II} ions is 3.593(1) Å and this suggests ferromagnetism for the compound [the room-temperature paramagnetic moment for (**2**) is 1.58 B.M.; for (**1**) and (**3**) this value is *ca.* 1.8 B.M., indicating them to be magnetically dilute].

In another compound, $[Cu(plimpa)]\cdot H_2O$ [$H_2plimpa$ = (pyridoxylideneiminomethyl)phosphonic acid],[15] where a square-pyramidal environment for the metal is observed, the molecule is a dimer due to the bridging of phenolic oxygen. The latter acts as a basal and axial donor for two Cu^{II} ions [as in (**2**)] at distances of 1.894 and 2.663 Å respectively with the Cu–Cu distances being 3.488 Å. As in (**3**), in (**2**), also, the equatorial plane involving the atoms O(1), O(3), N(2), and N(3) has slight tetrahedral deviations for these atoms (−0.023 to 0.024 Å). This plane makes a dihedral angle of 9.89° with the pyridine ring.

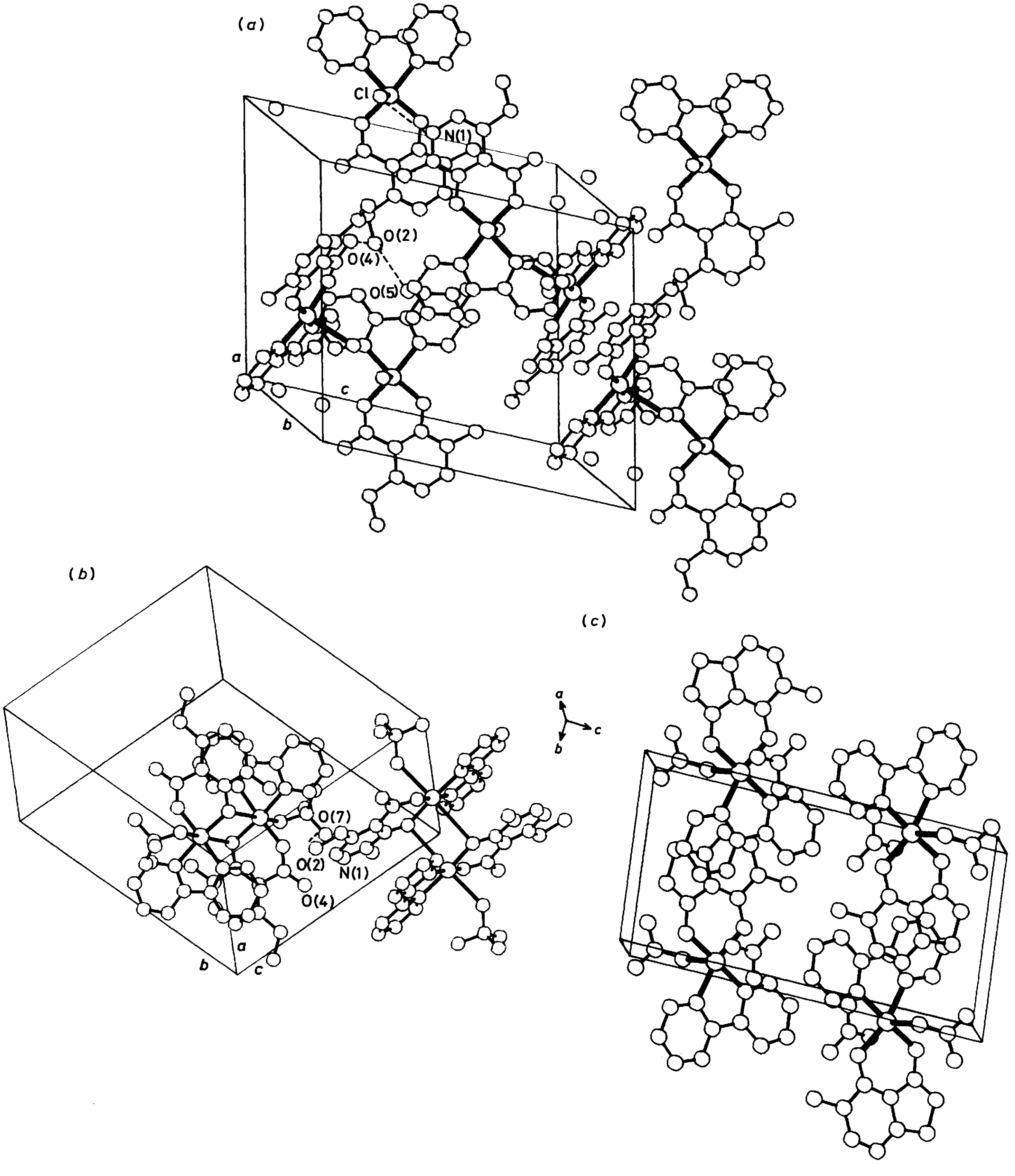

Figure 4. Packing diagrams of the compounds: (*a*) (**1**), (*b*) (**2**), (*c*) (**3**). Broken lines indicate possible hydrogen bonds

The equatorial bond lengths, 1.892—2.012 Å for (**1**) and 1.893—1.994 Å for (**2**), are normal. In (**3**), Cu–O(1) [1.945(3) Å] and Cu–O(3) [1.994(4) Å] are longer than normally observed in other vitamin B_6 complexes.[13] The long Cu–O(3) distance is indicative of the carbonyl nature of O(3). The axial Cu–Cl bond length [2.659(1) Å] in (**1**) is normal and is in the range observed for Cu^{II} compounds having Cl at the axial site.[5,16] The corresponding Cu–O(4) bond length is 2.388(4) Å in (**3**). The *cis* bond angles in the basal plane are in the range 80.7—92.5° for (**1**) and 80.9—96.4° for (**3**). The *trans* angles are 166.0 and 166.3° in (**1**), and 165.0 and 176.4° in (**3**). The axial bond makes angles of 91.7—101.4° with the equatorial bonds in (**1**) and 91.0—95.4° in (**3**). The *cis* bond angles around Cu in (**2**) are in the range 81.6—95.4° and the *trans* angles are 173.3, 175.4, and 172.2°.

Table 4. Possible hydrogen bonds[a]

Compound	Y–H···Z	Y–H/Å	Y···Z/Å	H···Z/Å	YHZ/°
(1)	N(1)–H(1)···Cl^{i}	0.96(5)	3.039(3)	2.10(5)	167(4)
	O(2)–H(8)···O(4^{ii})	0.86(6)	2.642(5)	1.80(5)	166(6)
	O(5)–H(17)···O(2^{i})	1.02(6)	2.765(6)	1.77(5)	166(6)
	O(5)^{b}···O(6^{iii})		2.811(7)		
	O(6)–H(18)···O(5)	1.05(9)	2.741(7)	1.71(9)	165(7)
(2)	N(1)–H(1)···O(4^{iv})	1.00(8)	2.668(7)	1.67(7)	172(7)
	O(2)^{c}···O(7^{v})		2.93(1)		
(3)	N(1)–H(1)···O(9^{vi})	0.87(7)	2.784(5)	1.94(7)	165(8)

[a] Symmetry superscripts: (i) $-x, 1 - y, -z$; (ii) $-0.5 - x, 0.5 + y, -0.5 - z$; (iii) $1 - x, 1 - y, -z$; (iv) $x, 0.5 - y, -0.5 + z$; (v) $-1 + x, 0.5 - y, -0.5 + z$; (vi) $1 + x, 1 + y, z$. [b] One hydrogen atom on O(5) was not located. [c] Hydrogen atom on O(2) was not located.

In all the complexes, there is one six-membered chelate ring and one five-membered chelate ring. The latter is virtually planar. The former assumes a 'sofa' conformation in (1) and (3), the deviations of Cu^{II} from the plane containing the rest of the atoms being 0.2957(6) and 0.243(1) Å respectively. In (2), however, the ring exhibits a chair conformation.[17]

Ligands. Depending on the sites of protonation or deprotonation the known structures of vitamin B$_6$ compounds and their metal complexes fall into four categories.[5] In the present compounds, the vitamin B$_6$ moieties (pa and pal) exist as neutral zwitterions (dipolar form) as far as phenolic oxygen and pyridine nitrogen are concerned. The carboxylate group of pa at the 4-position serves as the negatively charged donor. The other positive charge of Cu^{II} is neutralized by the chloride ion in (1) and perchlorate ion in (2). In (3), as pal is neutral, the positive charges are balanced by two nitrate anions.

(*i*) *Dimensions in pa and pal.* The bond lengths and angles of pa and pal moieties are normal and are comparable with those of the other compounds of B$_6$ vitamins.[13] The C(2)–O(1) distances of 1.296(5) Å in (1) and 1.308(8) Å in (2) are consistent with a deprotonated phenolic C–O bond. However, that in (3), 1.287(5) Å, is shorter than normal and is comparable with those observed in pyridoxylidene Schiff-base complexes.[13a] As explained earlier, this may be an indication of greater involvement of the electron cloud of O$^-$ in the pyridine ring delocalization. This deduction is also reflected in the elongated Cu–O(1) coordinated distance [1.945(3) Å], in (3), as compared to *ca.* 1.892(4) Å in (1) and (2).

The lactone ring in (3), even though similar to the hemiacetal ring of Hpl,[18] exhibits some special features. The two C–O distances in the ring are very different from each other, whereas in Hpl they are nearly equal. While the C(7)–O(2) bond length is 1.346(6) Å, with more double-bond character due to possible resonance with the carbonyl bond [note that C(7)–O(3) is increased, *cf.* (1) and (2), to 1.277(5) Å]; the C(8)–O(2) distance is 1.478(5) Å, indicative of more single-bond character. This difference can also be a result of the different nature of orbitals involved, namely *sp*^{2} of C(7) and *sp*^{3} of C(8). Moreover, the ring is almost planar (deviations −0.008 to 0.012 Å), whereas in Hpl[18] the ring exhibits envelope conformation with O(2) being out of the plane by 0.24 Å. This plane makes an angle of 0.67° with that of the pyridine ring.

(*ii*) *Bipyridyl.* The bipy ligands have normal bond lengths and angles as observed in similar compounds.[5,19] The individual ring of each bipy is planar (absolute deviations $\leqslant 0.018$ Å from the best plane); however, the two rings of a molecule assume their customary tilt, the dihedral angle between the planes of the rings being 4.56, 2.13, and 6.34° in (1), (2), and (3) respectively.

(*iii*) *Anions.* The co-ordinated perchlorate group in (2) has normal bond lengths and angles. It is relatively well fixed in the lattice due to its involvement in co-ordination as well as in hydrogen bonding, as compared to that in [Co(bipy)$_2$(pn)][ClO$_4$]$_2$ and [Cu(bipy)(Hpn)Cl]ClO$_4$·H$_2$O.[5] In (3), the co-ordinated nitrate plane is inclined to the co-ordination plane by 16.1°. Interestingly, the Cu^{II} ion lies 2.100(1) Å away from the plane of the co-ordinated nitrate. Such a situation has been previously observed in the case of [Cu(Hpm)$_2$(NO$_3$)$_2$]·H$_2$O[20] where it was pointed out that this kind of non-coplanarity is quite unusual for two reasons: (*i*) maximum orbital overlap between the lone pairs on donor oxygen and the orbitals on the Cu^{II} ions is achieved when the Cu^{II} ions are in the same plane as the nitrate group and (*ii*) coplanarity would minimize any steric crowding of the nitrate group with the Cu(Hpm)$_2$ moieties. Apparently other factors, like packing, seem to have a role in deciding the orientation of the nitrate group.

Molecular packing and hydrogen bonding. As is the the case of most of the vitamin B$_6$ complexes, the pyridine nitrogen N(1) is a proton donor in the present compounds also (Table 4, Figure 4). In (1), it is hydrogen-bonded to the co-ordinated chloride ion, as also observed in [Cu(bipy)(Hpn)Cl]ClO$_4$·H$_2$O.[5] Carboxylate oxygen O(4) and nitrate oxygen O(6) are the proton acceptors in (2) and (3) respectively. In (3), there is no other hydrogen bond, as the usual proton donor O(2) is a part of the lactone moiety. However, O(2) is involved in one hydrogen bond in (2) and two in (1). The water molecules in the lattice of (1) have the usual hydrogen-bond interactions (Table 4).

Apart from the hydrogen bonds, stacking interactions involving π-aromatic groups have been observed in two of the compounds. In (2), interestingly, there is partial stacking between the pyridine and one of the bipy rings within a dimeric unit (Figure 2). These rings have a dihedral angle of 11.25°, with the average distance of the atoms of one ring from the plane of the other being 3.52 Å. In (3) also, stacking is between the pyridine and bipy rings, but of molecules related by unit translation along *b* (Figure 4). The dihedral angle between the rings and the average distance of the atoms from the stacking plane are 5.67° and 3.49 Å respectively. However, it may be noted that a continuous stacking of the rings in the unit cell is not observed in either of these compounds. In (2), it has been restricted to within a dimeric unit, whereas in (3), pairs of molecules extending along the [010] direction are related by stacking interactions. No stacking is observed in (1).

Formation of the Compounds.—The unexpected formation of the compounds has been explained by a mechanism[8] where the initiation of the reaction comes from nucleophilic attack by the 5-hydroxymethyl oxygen on a carbonyl carbon atom. The absence of any role for the amino acid in such a reaction has been confirmed by our recent studies where similar complexes of pa have been obtained[21] even in the absence of the amino acid. Further work is in progress to understand the intricacies of this novel reaction. Attempts to obtain ternary Schiff-base complexes by alternative means are also underway.

Acknowledgements

We are grateful to Professor R. Bau, University of Southern California, Los Angeles, U.S.A., for providing *X*-ray data for compound (**2**). S. P. S. R. thanks the Department of Atomic Energy, India, for financial assistance. Part of this work was supported by the Indian National Science Academy.

References

1 D. E. Metzler and E. E. Snell, *J. Am. Chem. Soc.*, 1952, **74**, 979; J. B. Longenecker and E. E. Snell, *ibid.*, 1957, **79**, 142.

2 R. H. Holm, in 'Inorganic Biochemistry,' ed. G. L. Eichhorn, Elsevier, New York, 1973, pp. 1137—1167.

3 D. E. Metzler, *Adv. Enzymol. Relat. Areas Mol. Biol.*, 1979, **50**, 1.

4 A. E. Martell, *Adv. Enzymol. Relat. Areas Mol. Biol.*, 1982, **53**, 163.

5 S. P. S. Rao, K. I. Varughese, and H. Manohar, *Inorg. Chem.*, 1986, **25**, 734.

6 A. E. Martell, in 'Metal Ions in Biological Systems,' ed. H. Sigel, Dekker, New York, 1973, vol. 2, pp. 207—268.

7 H. C. Dunathan, *Adv. Enzymol. Relat. Areas Mol. Biol.*, 1971, **35**, 79.

8 S. P. S. Rao, H. Manohar, K. Aoki, H. Yamazaki, and R. Bau, *J. Chem. Soc., Chem. Commun.*, 1986, 4.

9 A. C. T. North, C. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

10 L. Casella and M. Gullotti, *J. Am. Chem. Soc.*, 1981, **103**, 6338; 1983, **105**, 803; L. Casella, M. Gullotti, and G. Pacchioni, *ibid.*, 1982, **104**, 2386.

11 M. E. Farago, M. M. McMillan, and S. S. Sabir, *Inorg. Chim. Acta*, 1975, **14**, 207; J. T. Wrobleski and G. J. Long, *Inorg. Chem.*, 1977, **16**, 2752; F. Nepveu, J. J. Bonnet, and J. P. Laurent, *J. Coord. Chem.*, 1981, **11**, 185.

12 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1978.

13 (*a*) S. P. S. Rao, H. Manohar, and R. Bau, *J. Chem. Soc., Dalton Trans.*, 1985, 2051; (*b*) ref. 5 and refs. therein.

14 A. Mosset, F. Nepveu-Juras, R. Haran, and J. J. Bonnet, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1259.

15 M. Darriet, A. Cassiagne, J. Darriet, and N. Neuzil, *Acta Crystallogr., Sect. B*, 1978, **34**, 2105.

16 C. J. Neitzel and R. Desiderato, *Cryst. Struct. Commun.*, 1975, **4**, 333; E. Sletten and A. Apeland, *Acta Crystallogr., Sect. B*, 1975, **31**, 2019; K. Aoki and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, 1984, 410.

17 W. L. Duax, C. M. Weeks, and D. C. Rohrer, in 'Topics in Stereochemistry,' eds. N. L. Allinger and E. L. Eliel, Wiley, New York, 1976, vol. 9, pp. 279-286.

18 S. P. S. Rao, M. D. Poojary, and H. Manohar, *Curr. Sci.*, 1982, **51**, 410.

19 G. Nardin, L. Randaccio, R. P. Bonomo, and E. J. Rizzarelli, *J. Chem. Soc., Dalton Trans.*, 1980, 369; J. Foley, D. Kennefick, D. Phelan, S. Tyagi, and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1983, 2333.

20 K. J. Franklin and M. F. Richardson, *Inorg. Chem.*, 1980, **19**, 2107.

21 S. P. S. Rao, I. I. Mathews, and H. Manohar, unpublished work.

Received 11th June 1986; *Paper* 6/1185