Inorganica Chimica Acta, 186 (1991) 253–261

X-ray studies on metal ion interactions with vitamins II*. Crystal structures of three copper(II) and nickel(II) complexes of Schiff bases formed between 1-aminocyclopropanecarboxylic acid and pyridoxal or pyridoxal 5′-phosphate

Katsuyuki Aoki**

Department of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441 (Japan)

Ninghai Hu and **Hiroshi Yamazaki**

The Institute of Physical and Chemical Research, Wako-shi, Saitama 351-01 (Japan)

(Received January 17, 1991; revised April 16, 1991)

Abstract

The crystal structures of three Schiff base metal complexes of 1-aminocyclopropanecarboxylic acid (ACC), a precursor of the plant hormone ethylene, $[Cu(PL\text{-}ACC)(H_2O)]\cdot(NO_3)\cdot H_2O$ (**1**), $[Ni(PL\text{-}ACC)(H_2O)_2]\cdot(NO_3)\cdot H_2O$ (**2**) and $[Cu(PLP\text{-}ACC)(H_2O)]_2\cdot 4H_2O$ (**3**) (PL = pyridoxal and PLP = pyridoxal 5′-phosphate), have been determined by X-ray diffraction. **1** and **2** are quasi-isostructural to each other, with a minor difference in the coordination geometry, i.e. square-pyramidal copper(II) and square-bipyramidal nickel(II): the basal plane is defined by the imino nitrogen, the phenolic and the carboxylate oxygens of the Schiff base ligand, and a water molecule, and the apical position(s) occupied by the hydroxymethyl oxygen of a neighboring molecule (plus a water for **2**), thus forming a one-dimensional polymer. **3** involves two crystallographically independent $[Cu(PLP\text{-}ACC)(H_2O)]$ structural units, A and B, which differ only in the phosphate conformation. The environment of each copper atom is similar to that in **1** except for the axial coordination of one of the phosphate oxygens of a neighboring molecule, thus creating an analogous polymeric chain structure, –A–B–A–B–. These three compounds may serve as a model for a Schiff base derived from pyridoxal and 1-aminocyclopropanecarboxylate, a reaction intermediate in ethylene biosynthesis, in accordance with Dunathan's hypothesis.

Cystallographic data: **1**, space group $P2_1/a$, $a = 13.222(3)$, $b = 10.820(2)$, $c = 11.821(3)$ Å, $\beta = 110.51(2)°$, $V = 1583.9(7)$ Å^3, $Z = 4$ and $R = 0.044$ for 2034 observed reflections; **2**, space group $P2_1/c$, $a = 12.896(2)$, $b = 10.667(2)$, $c = 12.628(3)$ Å, $\beta = 111.23(2)$, $V = 1619.3(6)$ Å^3, $Z = 4$ and $R = 0.043$ for 1603 observed reflections; **3**, space group $P\bar{1}$, $a = 15.700(2)$, $b = 11.738(1)$, $c = 9.281(1)$ Å, $\alpha = 98.61(1)$, $\beta = 97.34(1)$, $\gamma = 98.16(1)°$, $V = 1654.4(3)$ Å^3, $Z = 2$ and $R = 0.038$ for 4732 observed reflections.

Introduction

Pyridoxal 5′-phosphate (the cofactor form of vitamin B_6)-dependent enzymes catalyze a variety of metabolic reactions of amino acids such as decarboxylation, transamination, racemization, or C–C cleavage. Though metal ions are not required for these reactions in biological systems, many of these reactions can be duplicated by metal ions in the presence of pyridoxal with similar mechanisms, where the metal ion could act as a trap of a Schiff base intermediate derived from pyridoxal and amino acid and also exerts its electronic effects to promote the subsequent reactions [2]. Despite the importance of the stereochemistry of the Cα atom in the amino acid residue in controlling the activity of the Schiff base [3], however, only a limited number of crystal structures of metal–pyridoxal Schiff base complexes are available [4]. As a continuation of our X-ray investigations [4d, h] we report here three crystal structures of the copper(II) or nickel(II) complexes formed between 1-aminocyclopropanecarboxylic acid (ACC) and pyridoxal (PL) or pyridoxal 5′-phosphate (PLP): $[Cu(PL\text{-}ACC)(H_2O)]\cdot(NO_3)\cdot H_2O$ (**1**), $[Ni(PL\text{-}ACC)(H_2O)_2]\cdot(NO_3)\cdot H_2O$ (**2**) and $[Cu(PLP\text{-}ACC)(H_2O)]_2\cdot 4H_2O$ (**3**). ACC, a rare amino acid, is well known as a precursor of the plant hormone

---

*Part I is ref. 1.

**Author to whom correspondence should be addressed.

0020-1693/91/$3.50

TABLE 1. Crystal and refinement data

Compound	1	2	3
Formula	$C_{12}H_{17}CuN_3O_9$	$C_{12}H_{19}N_3NiO_{10}$	$C_{24}H_{38}Cu_2N_4O_{20}P_2$
Molecular weight	410.82	424.01	891.62
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/a$	$P2_1/c$	$P\bar{1}$
a (Å)	13.222(3)	12.896(2)	15.700(2)
b (Å)	10.820(2)	10.667(2)	11.738(1)
c (Å)	11.821(3)	12.628(3)	9.281(1)
α (°)			98.61(1)
β (°)	110.51(2)	111.23(2)	97.34(1)
γ (°)			98.16(1)
V (Å^3)	1583.9(7)	1619.3(6)	1654.4(3)
Z	4	4	2
D_c (g cm^{-3})	1.72	1.74	1.79
$F(000)$	844	880	916
μ(Mo Kα) (cm^{-1})	14.33	12.61	14.73
Crystal color	dark green	blue green	green
Crystal shape	rectangular	column	plate
Crystal size (mm)	0.13×0.23×0.51	0.07×0.11×0.38	0.22×0.34×0.40
Transmission factors[a]	0.92–1.07	0.96–1.03	0.95–1.11
T (K)	293	293	293
Reflections measured	$\pm h, +k, +l$	$\pm h, +k, +l$	$\pm h, \pm k, +l$
Scan type	ω for $2\theta \leqslant 30°$ ω–2θ for $2\theta > 30°$	ω–2θ	ω–2θ
2θ Range (°)	3.0–50.0	3.0–50.0	3.0–50.0
Scan speed (° min^{-1})	4.0	4.0	4.0
Scan range (°)	$1.2+0.5 \tan \theta$	$1.4+0.5 \tan \theta$	$1.2+0.5 \tan \theta$
Background counting (s)	5 at the lower and upper limits of each scan		
Total no. unique reflections	2881	2945	5754
No. observed reflections (m) with $F_o > 3\sigma(F_o)$	2034	1603	4732
Variables (n)	321	288	574
Weighting scheme (w)	$\sigma(F_o)^{-2}$	1.0 for $F_o \leqslant 100$ $10^4/F_o^2$ for $F_o > 100$	1.0 for $F_o \leqslant 100$ $10^4/F_o^2$ for $F_o > 100$
R[b]	0.044	0.043	0.038
R_w[c]	0.045	0.046	0.042
S[d]	1.58	1.87	1.51
Max. peak in the final difference Fourier map (e Å^{-3})	0.55	0.44	0.63

[a] Normalized to an average of unity. [b] $R=\Sigma|F_o-|F_c||/\Sigma F_o$. [c] $R_w=[\Sigma w(F_o-|F_c|)^2/\Sigma wF_o^2]^{1/2}$. [d] $S=[\Sigma w(F_o-|F_c|)^2/(m-n)]^{1/2}$.

ethylene and is biosynthesized from (*S*)-adenosylmethionine by PLP-dependent synthase (ACC synthase), via formation of the *N*-(pyridoxylidene[†])-1-aminocyclopropanecarboxylate Schiff base intermediate [5]. The present complexes serve as a model for such a reaction intermediate, in accordance with Dunathan's hypothesis [3]. The structure of **1** has been reported in brief [6]. To our knowledge, **3** is only the third example [4b, i] of a metal–PLP complex and the sixth [4b, i, 7] of a PLP derivative.

Experimental

Preparations

The compounds were prepared from ACC, PL·HCl or PLP·H_2O and $Cu(NO_3)_2 \cdot 3H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$, each with a 1:1:1 molar ratio in an aqueous solution at room temperature (pH: *c.*

[†] 3-Hydroxy-5-hydroxymethyl-1-methyl-4-pyridylmethylene group is tentatively named pyridoxylidene.

4 for **1**, *c.* 3 for **2**, *c.* 2 for **3**). *Anal.* Found for **1**: C, 34.73; H, 4.13; N, 10.16. Calc. for $C_{12}H_{17}CuN_3O_9$: C, 35.08; H, 4.17; N, 10.23%. Found for **2**: C, 33.90; H, 4.53; N, 9.88. Calc. for $C_{12}H_{19}N_3NiO_{10}$: C, 33.99; H, 4.52; N, 9.91%. Found for **3**: C, 32.18; H, 4.19; N, 6.21. Calc. for $C_{12}H_{19}CuN_2O_{10}P$: C, 32.33; H, 4.30; N, 6.28%.

X-ray analysis

Cell constants were determined on a Rigaku AFC-5 automatic diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) from 20 high-order reflections (2θ: 22–32° for **1**, 19–32° for **2**, 26–34° for **3**). Details of the crystal data and data collection together with structure refinement are summarized in Table 1. Throughout the data collection, the intensities of the three standard reflections were monitored every 100 or 150 measurements; a maximum variation in intensity less than of 2% was noted for **2**. Intensities were corrected for Lorentz and polarization effects, but not for absorption because of the small variations in intensity of an axial reflection (at $\chi \sim 90°$) with the spindle angle ϕ.

TABLE 2. Atomic parameters ($\times 10^5$ for Cu and $\times 10^4$ for other atoms) for **1**

Atom	*x*	*y*	*z*
Cu	13416(5)	18957(5)	14303(6)
O(1)	1942(3)	3295(3)	849(3)
O(2)	2074(3)	5355(3)	943(3)
O(3′)	661(3)	576(3)	1925(3)
O(5′)	−2072(3)	3484(3)	3093(4)
N(1)	−933(3)	−514(4)	3544(4)
N(2)	667(3)	3149(3)	2114(3)
C(2)	−309(4)	−515(4)	2874(5)
C(3)	43(4)	645(4)	2549(4)
C(4)	−300(4)	1740(4)	2963(4)
C(5)	−994(4)	1661(4)	3648(4)
C(6)	−1285(4)	523(5)	3940(5)
C(7)	1719(4)	4355(4)	1178(4)
C(8)	958(4)	4388(4)	1869(4)
C(9)	1050(4)	5425(5)	2752(5)
C(10)	134(4)	5421(5)	1597(5)
C(2′)	7(5)	−1703(5)	2472(6)
C(4′)	32(4)	2962(4)	2700(4)
C(5′)	−1404(4)	2798(5)	4111(5)
O(W1)	1726(4)	647(4)	440(4)
O(W2)	1557(5)	−1927(4)	378(5)
N(3)	−1749(4)	−3547(4)	4074(4)
O(31)[a]	−1893(5)	−2463(5)	4231(6)
O(32)[a]	−2402(4)	−4350(5)	4155(5)
O(33)[a]	−924(5)	−3943(7)	3928(8)
O(34)[a]	−2022(10)	−4402(11)	4571(10)
O(35)[a]	−1751(21)	−3541(20)	2990(17)
O(36)[a]	−1517(13)	−2539(13)	4666(12)

[a] These oxygen atoms are disordered; occupancy factors, 0.7 for O(31)–O(33) and 0.3 for O(34)–O(36).

TABLE 3. Atomic parameters ($\times 10^5$ for Ni and $\times 10^4$ for other atoms) for **2**

Atom	*x*	*y*	*z*
Ni	14619(6)	15712(7)	14534(6)
O(1)	1005(3)	3037(4)	2205(3)
O(2)	1006(3)	5116(4)	2318(3)
O(3′)	1984(3)	280(4)	641(3)
O(5′)	2975(3)	3611(4)	−2072(3)
N(1)	3682(4)	−534(5)	−906(4)
N(2)	2052(4)	2956(4)	746(4)
C(2)	3066(5)	−643(6)	−259(5)
C(3)	2626(5)	458(6)	60(5)
C(4)	2901(4)	1641(6)	−285(4)
C(5)	3552(4)	1668(6)	−1002(4)
C(6)	3915(5)	580(6)	−1287(5)
C(7)	1223(5)	4122(6)	1931(5)
C(8)	1781(5)	4186(5)	1060(5)
C(9)	1425(5)	5227(6)	191(5)
C(10)	2519(5)	5300(6)	1109(5)
C(2′)	2853(6)	−1912(6)	116(6)
C(4′)	2587(5)	2830(5)	73(5)
C(5′)	3902(5)	2858(6)	−1415(5)
O(W1)	926(3)	194(4)	2276(3)
O(W2)	−136(3)	1552(4)	207(3)
O(W3)	590(4)	7611(4)	1891(4)
N(3)	4232(5)	6445(6)	−1771(5)
O(31)	4668(4)	7478(5)	−1620(5)
O(32)	3306(6)	6309(8)	−1744(8)
O(33)	4666(6)	5535(5)	−2006(7)

The structures were straightforwardly solved by the heavy-atom method for **1** and **2**, while for **3** by the combination of the heavy-atom method and MULTAN78 [8] with some difficulty because of high correlations between the atomic positions of the two crystallographically independent molecules. The structures were refined by block-diagonal least-squares method, minimizing the function $\Sigma w(F_o - |F_c|)^2$. Thermal parameters of all non-hydrogen atoms (including disordered nitrate oxygens with occupancy factors of 0.7 for O(31)–O(33) and 0.3 for O(34)–O(36) in **1**) were refined anisotropically. Hydrogen atoms were located from difference Fourier maps; they were isotropically refined for **1**, while those attached to waters were fixed ($B = 5$ Å^2) and the others isotropically refined for **2** and **3**.

Programs used and sources of neutral atomic scattering factors are given in ref. 1. The final atomic coordinates are listed in Tables 2–4 for **1**–**3**, respectively.

Results and discussion

Description of the structures

Compounds 1 and 2

The molecular structures and atomic numbering of the complexes **1** and **2** are shown in Figs. 1 and

TABLE 4. Atomic parameters (×10^5 for Cu and ×10^4 for other atoms) for **3**

Atom	*x*	*y*	*z*
Cu(A)	13962(3)	7351(4)	18506(5)
P(5′A)	4997(1)	2544(1)	6818(1)
O(1A)	920(2)	−833(2)	2115(3)
O(2A)	586(1)	−1881(2)	3816(3)
O(3′A)	2087(2)	2153(3)	1622(3)
O(5′A)	3993(2)	2584(2)	6942(3)
O1(P5′A)	5116(2)	1334(2)	7000(3)
O2(P5′A)	5566(2)	3543(2)	7848(3)
O3(P5′A)	5102(2)	2763(2)	5199(3)
O(W1A)	1095(2)	388(3)	−311(3)
N(1A)	3618(2)	4686(3)	3147(4)
N(2A)	1841(2)	957(3)	3951(3)
C(2A)	3074(3)	3884(3)	2161(4)
C(3A)	2614(2)	2899(3)	2631(4)
C(4A)	2779(2)	2817(3)	4155(4)
C(5A)	3389(2)	3691(3)	5127(4)
C(6A)	3783(3)	4620(3)	4600(4)
C(7A)	948(3)	−980(3)	3460(4)
C(8A)	1453(2)	1(3)	4598(4)
C(9A)	1896(3)	−295(4)	6005(4)
C(10A)	1118(3)	272(4)	6061(5)
C(2′A)	2989(3)	4018(4)	577(5)
C(4′A)	2365(2)	1823(3)	4727(4)
C(5′A)	3628(3)	3629(4)	6743(4)
Cu(B)	64045(3)	6688(4)	66071(5)
P(5′B)	9885(1)	2547(1)	12475(1)
O(1B)	5878(2)	−933(2)	6694(3)
O(2B)	5605(2)	−2148(3)	8254(4)
O(3′B)	7160(2)	2086(2)	6510(3)
O(5′B)	8849(2)	2390(2)	12050(3)
O1(P5′B)	10089(2)	1351(2)	12078(3)
O2(P5′B)	10312(2)	3498(3)	11783(3)
O3(P5′B)	10072(2)	2988(3)	14194(3)
O(W1B)	6126(2)	375(3)	4453(3)
N(1B)	8700(2)	4529(3)	8340(4)
N(2B)	6799(2)	752(3)	8700(3)
C(2B)	8185(3)	3773(3)	7258(4)
C(3B)	7661(2)	2775(3)	7596(4)
C(4B)	7749(2)	2632(3)	9102(4)
C(5B)	8313(2)	3473(3)	10190(4)
C(6B)	8777(3)	4412(3)	9785(4)
C(7B)	5921(3)	−1196(4)	8006(4)
C(8B)	6404(3)	−262(3)	9233(4)
C(9B)	6835(3)	−640(4)	10590(5)
C(10B)	6045(3)	−111(4)	10689(5)
C(2′B)	8191(3)	3997(4)	5719(5)
C(4′B)	7300(3)	1604(4)	9564(4)
C(5′B)	8434(3)	3384(4)	11808(4)
O(W3)	5801(3)	3424(5)	10936(5)
O(W4)	6507(3)	2420(4)	3257(4)
O(W5)	10682(2)	2522(3)	8970(4)
O(W6)	11473(3)	3689(4)	6865(5)

2, respectively, and the packing diagrams in Figs. 3 and 4. Bond distances and angles are given in Table 5.

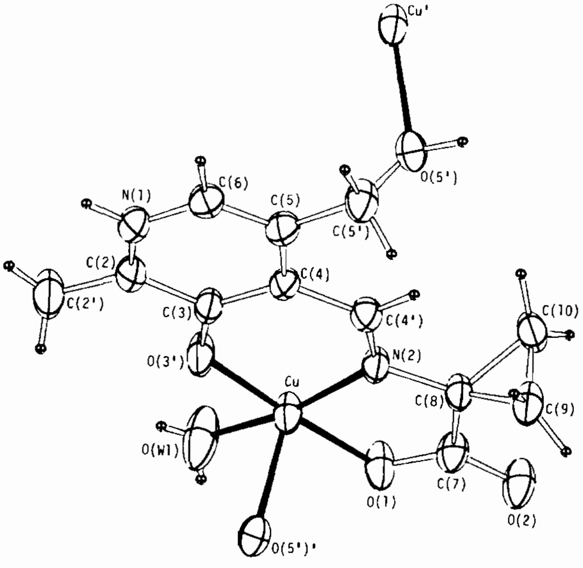

Fig. 1. Molecular structure of **1**.

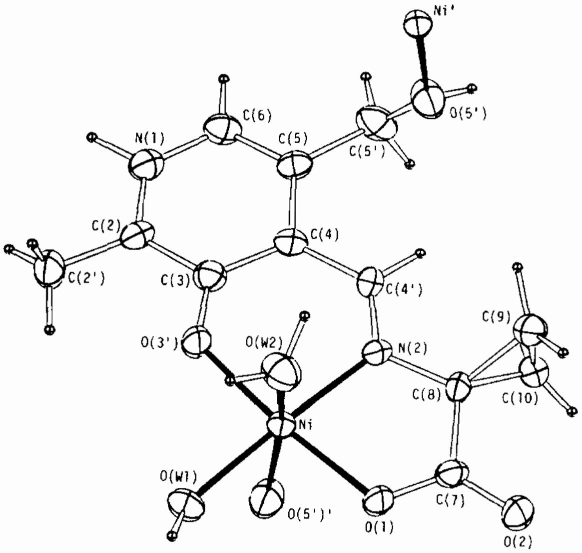

Fig. 2. Molecular structure of **2**.

In each compound, the pyridoxal moiety forms a Schiff base with ACC, as expected. The tetradentate Schiff base, which exists as a monovalent anion with the carboxylate and the phenolate groups deprotonated and the ring nitrogen N(1) protonated, coordinates to the square-pyramidal copper or the square-bipyramidal nickel atom through the carboxylate O(1) and the phenolate oxygens and the imino nitrogen N(2), as do other known metal complexes of pyridoxal–amino acid Schiff bases, and the fourth basal donor is a water molecule; the axial position(s) is occupied by the hydroxymethyl oxygen O(5′) from a neighboring molecule (plus a water molecule for **2**), thus producing a one-dimensional

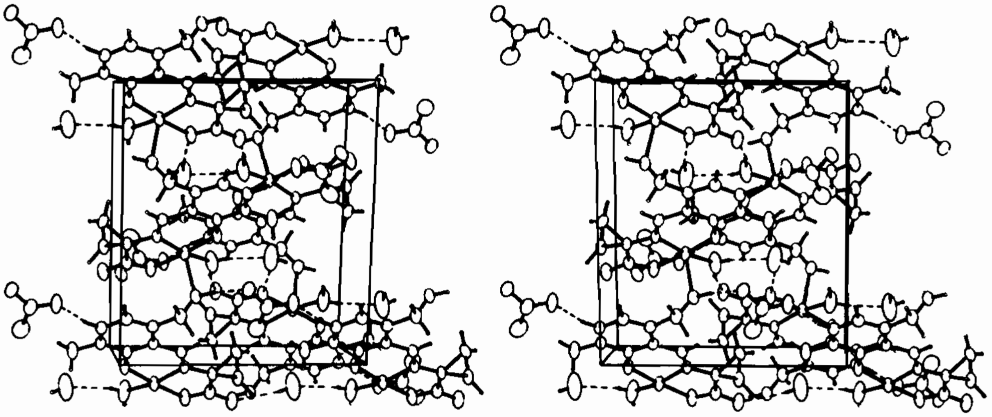

Fig. 3. A stereoscopic view showing the crystal packing of **1**, viewed down the *c* axis with the *b* axis being horizontal and the *a* axis vertical. Broken lines denote hydrogen bonds.

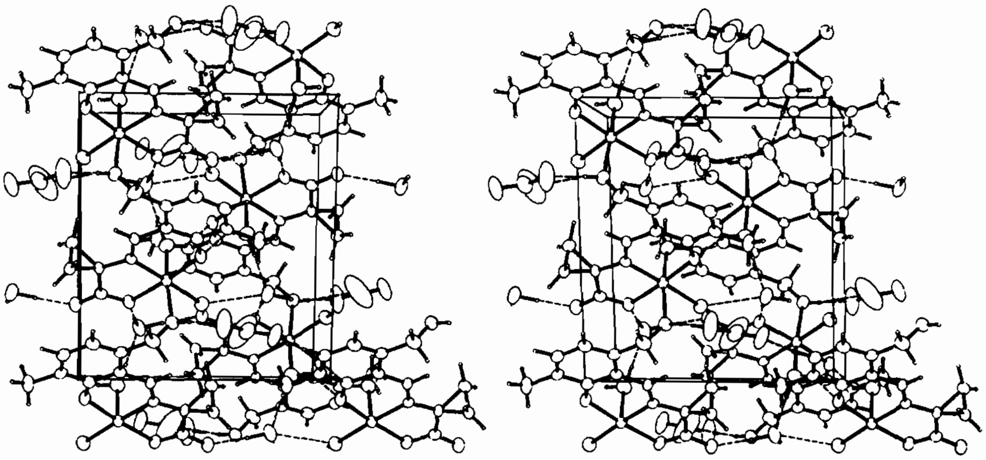

Fig. 4. A stereoscopic view showing the crystal packing of **2**, viewed down the *a* axis with the *b* axis horizontal and the *c* axis vertical. Broken lines denote hydrogen bonds.

polymer. Ligation through the hydroxymethyl oxygen is not generally unusual but it is very rare for pyridoxal with only one [4f] example known, whereas for pyridoxine [9] the hydroxymethyl oxygen at C(4), but not at C(5), is a common metal binding site. The pyridoxal–imine (pyridoxal + imino nitrogen N(2)) moiety and the α-carbon atom C(8) are almost in the square plane (O(1), N(2), O(3′), O(W1)); the carboxylato group is also nearly in this plane with the C(4′)–N(2)–C(8)–C(7) torsion angle being 179.5(4)° for **1** and −175.7(5)° for **2**.

The crystal packings are essentially the same in both **1** and **2**. Molecular columns composed of polymeric molecular chains are connected to one another through hydrogen bonds involving water ligands, nitrate anions and waters of crystallization (Tables 7 and 8, see 'Supplementary material'). The following hydrogen-bonding pattern is common to **1** and **2**: the basal coordination water O(W1) donates a hydrogen to the carboxylato O(2) of a neighboring column and another hydrogen to the lattice water, O(W2) in **1** or O(W3) in **2**, which in turn participates in hydrogen bonding with the O(1) of the same carboxylato group and with the carboxylato O(2) of another different column; a nitrate anion bridges between two columns via an N(1)–H...O(31)–N(3)–O(32)(–O(33) in **2**)...H–O(5′) hydrogen-bonding chain. An apical water ligand O(W2) in **2**, which is missing in **1**, adds two hydrogen bonds: one with the lattice water O(W3) and another with the phenolate O(3′). The polymeric structure itself is further stabilized by an electrostatic interaction between the carboxylate planar anion and the pyridinium ring, with a parallel arrangement (average spacing = 3.33 and 3.19 Å for **1** and **2**, respectively, and closest contact = 3.279(5) Å between O(2) and N(1′) for **1** and 3.245(6) Å between O(1) and C(4′) for **2**).

Compound 3

Figure 5 shows the molecular structure of the complex. Bond distances and angles are listed in

TABLE 5. Bond distances (Å) and angles (°) for **1** and **2**

	1	**2**		**1**	**2**
Coordination sphere M	Cu(II)	Ni(II)		Cu(II)	Ni(II)
M–O(1)	1.943(4)	2.024(4)	M–O(W1)	1.968(5)	2.058(5)
M–N(2)	1.947(4)	2.013(5)	M–O(5′)′	2.354(3)	2.163(4)
M–O(3′)	1.886(4)	1.976(5)	M–O(W2)		2.092(4)
N-(Pyridoxylidene)-1-aminocyclopropanecarboxylate ligand					
N(1)–C(2)	1.328(8)	1.335(9)	C(5′)–O(5′)	1.426(6)	1.431(7)
C(2)–C(3)	1.437(7)	1.424(9)	C(4′)–N(2)	1.279(7)	1.281(9)
C(3)–C(4)	1.417(7)	1.421(9)	N(2)–C(8)	1.451(6)	1.449(8)
C(4)–C(5)	1.423(8)	1.440(9)	C(8)–C(7)	1.502(9)	1.518(10)
C(5)–C(6)	1.369(7)	1.348(9)	C(7)–O(1)	1.279(6)	1.269(7)
C(6)–N(1)	1.359(7)	1.356(8)	C(7)–O(2)	1.249(6)	1.241(8)
C(2)–C(2′)	1.480(8)	1.492(9)	C(8)–C(9)	1.509(7)	1.512(8)
C(3)–O(3′)	1.281(8)	1.304(9)	C(8)–C(10)	1.515(7)	1.510(9)
C(4)–C(4′)	1.461(7)	1.453(9)	C(9)–C(10)	1.475(7)	1.468(8)
C(5)–C(5′)	1.521(8)	1.503(10)			
N(1)–C(2)–C(3)	119.1(5)	119.2(6)	C(6)–C(5)–C(5′)	118.1(5)	117.2(6)
C(2)–C(3)–C(4)	117.7(5)	118.4(6)	C(5)–C(5′)–O(5′)	108.2(4)	112.5(5)
C(3)–C(4)–C(5)	119.7(5)	118.5(6)	C(4′)–N(2)–C(8)	121.6(4)	121.2(5)
C(4)–C(5)–C(6)	119.4(5)	119.3(6)	N(2)–C(8)–C(7)	111.2(4)	112.5(5)
C(5)–C(6)–N(1)	119.7(6)	121.1(6)	N(2)–C(8)–C(9)	120.8(5)	120.4(5)
C(6)–N(1)–C(2)	124.4(5)	123.5(6)	N(2)–C(8)–C(10)	120.2(4)	120.9(6)
N(1)–C(2)–C(2′)	119.8(5)	119.5(6)	C(8)–C(7)–O(1)	117.1(5)	116.6(5)
C(3)–C(2)–C(2′)	121.2(6)	121.4(6)	C(8)–C(7)–O(2)	118.4(5)	118.8(6)
C(2)–C(3)–O(3′)	115.8(4)	116.0(6)	O(1)–C(7)–O(2)	124.4(6)	124.6(6)
C(4)–C(3)–O(3′)	126.5(5)	125.6(6)	C(7)–C(8)–C(9)	119.1(4)	117.4(5)
C(3)–C(4)–C(4′)	121.8(5)	123.4(6)	C(7)–C(8)–C(10)	118.1(4)	117.6(5)
C(5)–C(4)–C(4′)	118.5(5)	118.0(6)	C(9)–C(8)–C(10)	58.4(3)	58.1(4)
C(4)–C(4′)–N(2)	124.2(5)	125.2(6)	C(8)–C(9)–C(10)	61.1(3)	60.9(4)
C(4)–C(5)–C(5′)	122.5(5)	123.5(6)	C(8)–C(10)–C(9)	60.6(3)	61.0(4)

Table 6. (Hydrogen bonding and other short contacts are given in Table 9, see 'Supplementary material'.)

The complex involves the two crystallographically independent but chemically equivalent [Cu(PLP-ACC)(H_2O)] structure units, A and B, where each tetradentate Schiff base behaves as a divalent anion with the carboxylate, phenolate and phosphate groups each monovalently deprotonated and the ring nitrogen N(1) protonated. The coordination pattern is essentially the same as that in **1**, except that the axial position is occupied by the phosphate oxygen O1(P5′) of a neighboring molecule, thus creating an analogous one-dimensional polymeric structure which consists of an $(\text{–A–B–A–B–})_n$ molecular chain. Molecules A and B are almost related to each other by a pseudo symmetry of $\frac{1}{2}+x, y, \frac{1}{2}+z$; a major difference occurs in the conformation of the phosphate group (torsion angle C(5′)–O(5′)–P(5′)–O3(P5′) = –59.7(3) and 83.0(3)° for A and B, respectively, where O3(P5′) bears a hydrogen), possibly due to different hydrogen-bonding schemes around the phosphate group (see below). Here again each carboxylato group lies nearly in the pyridoxal–aldimine (C(4′)=N(2)–C(8)) plane: the torsion angle C(4′)–N(2)–C(8)–C(7) = –173.1(4) and –174.1(4)° for A and B, respectively.

The crystal packing is mainly determined by extensive hydrogen bonds (Fig. 6 and Table 9). $(\text{–A–B–A–B–})_n$ polymeric molecular chains, which are running along the $a+c$ direction, are connected to each other by inter-polymer hydrogen bonds and via water bridges. An $(\text{–A–B–A–B–})_n$ polymer chain is directly interlinked to three neighboring ones, which are centrosymmetrically related to each other and thus running antiparallelly; two chains (which are related by a center of inversion at 0, 0, 0) are joined directly by O(W1A)–H1...O1(P5′B), O(W1B)–H1...O1(P5′A) and O3(P5′A)–H...O(1B) hydrogen bonds and indirectly by water bridges involving O(W3), O(W4) and O(W5), two chains (at 0, 0, $-\frac{1}{2}$) directly by O3(P5′B)–H...O(2A) hydrogen bonds and indirectly by water bridges involving O(W3), O(W4), O(W5) and O(W6), and two chains

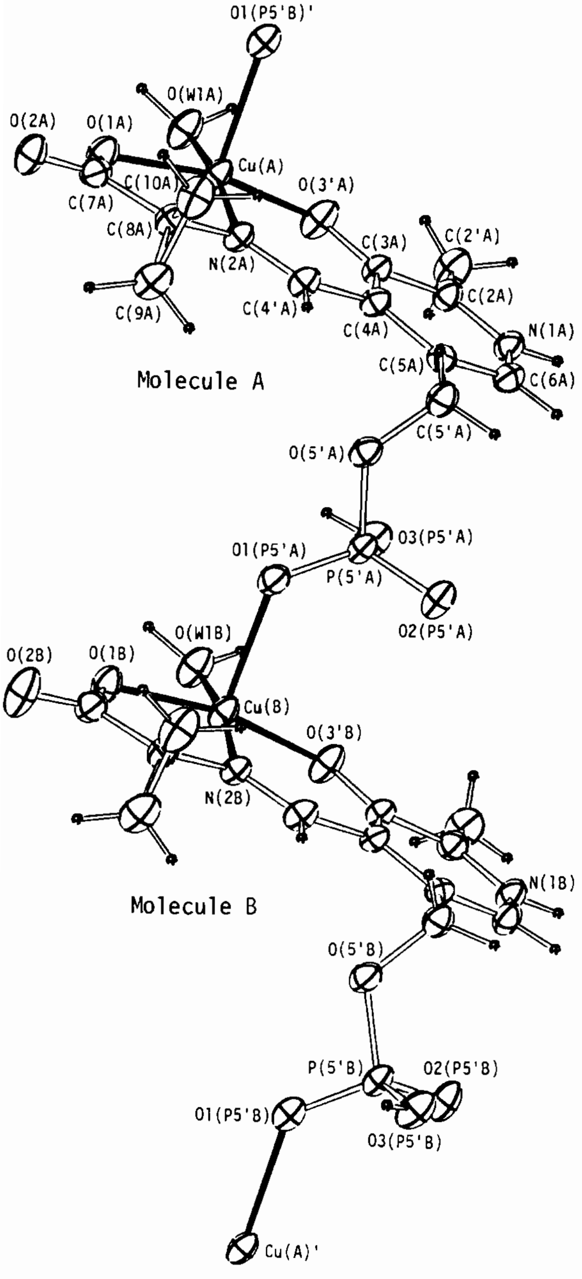

Fig. 5. Molecular structure of 3.

TABLE 6. Bond distances (Å) and angles (°) for 3

	Molecule	
	A	B
Coordination sphere		
Cu–O(1)	1.949(3)	1.962(3)
Cu–N(2)	1.951(3)	1.945(3)
Cu–O(3')	1.909(3)	1.922(3)
Cu–O(W1)	1.968(3)	1.958(3)
Cu–O1(P5')'	2.294(3)	2.321(3)
N-(5'-Phosphopyridoxylidene)-1-aminocyclopropane-carboxylate ligand		
N(1)–C(2)	1.328(4)	1.331(4)
C(2)–C(3)	1.429(6)	1.432(6)
C(3)–C(4)	1.425(6)	1.424(6)
C(4)–C(5)	1.417(5)	1.416(5)
C(5)–C(6)	1.363(6)	1.361(6)
C(6)–N(1)	1.357(5)	1.359(5)
C(2)–C(2')	1.493(6)	1.491(6)
C(3)–O(3')	1.295(4)	1.289(4)
C(4)–C(4')	1.457(6)	1.459(6)
C(5)–C(5')	1.514(6)	1.510(6)
C(5')–O(5')	1.451(5)	1.447(5)
O(5')–P(5')	1.603(3)	1.602(3)
P(5')–O1	1.490(3)	1.487(3)
P(5')–O2	1.495(3)	1.490(3)
P(5')–O3	1.586(3)	1.578(3)
C(4')–N(2)	1.273(4)	1.280(4)
N(2)–C(8)	1.446(5)	1.446(5)
C(8)–C(7)	1.494(5)	1.498(5)
C(7)–O(1)	1.281(5)	1.296(5)
C(7)–O(2)	1.238(5)	1.224(5)
C(8)–C(9)	1.510(6)	1.509(6)
C(8)–C(10)	1.523(6)	1.525(6)
C(9)–C(10)	1.473(7)	1.470(7)
N(1)–C(2)–C(3)	119.5(4)	119.7(4)
C(2)–C(3)–C(4)	117.5(3)	116.8(3)
C(3)–C(4)–C(5)	119.5(4)	120.2(4)
C(4)–C(5)–C(6)	119.4(4)	119.5(4)
C(5)–C(6)–N(1)	120.3(3)	119.8(3)
C(6)–N(1)–C(2)	123.8(4)	124.0(4)
N(1)–C(2)–C(2')	118.7(4)	117.9(4)
C(3)–C(2)–C(2')	121.8(3)	122.4(3)
C(2)–C(3)–O(3')	116.7(4)	117.1(3)
C(4)–C(3)–O(3')	125.8(4)	126.1(3)
C(3)–C(4)–C(4')	121.5(3)	121.8(3)
C(5)–C(4)–C(4')	119.0(3)	118.0(3)
C(4)–C(4')–N(2)	124.9(4)	125.1(4)
C(4)–C(5)–C(5')	122.3(4)	123.1(4)
C(6)–C(5)–C(5')	118.3(3)	117.4(3)
C(5)–C(5')–O(5')	111.7(3)	110.3(3)
C(5')–O(5')–P(5')	120.1(2)	120.3(2)
O(5')–P(5')–O1	104.7(2)	104.3(2)
O(5')–P(5')–O2	110.4(2)	110.0(2)
O(5')–P(5')–O3	105.1(2)	105.0(2)
O1–P(5')–O2	118.3(2)	118.3(2)
O1–P(5')–O3	111.2(2)	111.9(2)
O2–P(5')–O3	106.4(2)	106.7(2)
C(4')–N(2)–C(8)	121.8(3)	121.9(3)
N(2)–C(8)–C(7)	112.3(3)	112.3(3)
N(2)–C(8)–C(9)	121.1(3)	120.9(3)
N(2)–C(8)–C(10)	119.0(3)	119.9(3)
C(8)–C(7)–O(1)	116.3(4)	115.9(4)
C(8)–C(7)–O(2)	121.1(4)	120.8(4)
O(1)–C(7)–O(2)	122.7(3)	123.3(3)
C(7)–C(8)–C(9)	118.0(4)	117.8(4)
C(7)–C(8)–C(10)	118.4(3)	118.0(3)
C(9)–C(8)–C(10)	58.1(3)	58.0(3)
C(8)–C(9)–C(10)	61.4(3)	61.6(3)
C(8)–C(10)–C(9)	60.5(3)	60.5(3)

(at 0, $-\frac{1}{2}$, 0) directly by N(1A)–H...O2(P5'A) and N(1B)–H...O2(P5'B) hydrogen bonds (not shown in Fig. 6). Thus hydrogen-bonding systems about the two independent phosphate groups, A and B, are somewhat different, responsible for their different conformations.

Molecular dimensions of the 1-aminocyclopropane-carboxylate moiety

The present complexes give structural dimensions of the ACC molecule, which have been little known

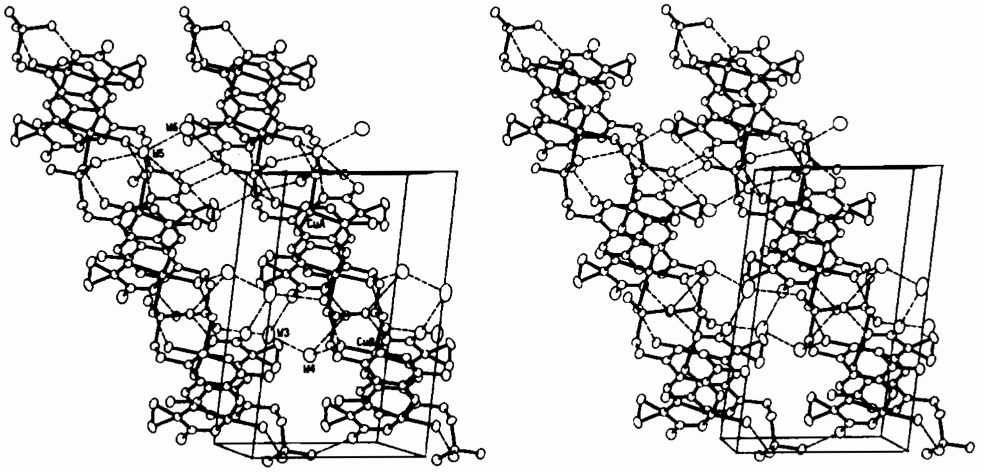

Fig. 6. A stereoscopic view showing the crystal packing of **3**, viewed down the *b* axis with the *c* axis horizontal and the *a* axis vertical. Broken lines denote hydrogen bonds.

despite its biological importance as a precursor of ethylene biosynthesis, except for those in *cis*-dichlorobis(ethyl 1-aminocyclopropanecarboxylato)platinum(II) [10], the only X-ray example for an ACC derivative so far reported. The three C–C bond distances and the three internal bond angles within the cyclopropane ring are not equivalent; the length of the 'back' ring bond [11a], C(9)–C(10) (1.475(7) Å in **1**, 1.468(8) Å in **2**, 1.470(7) and 1.473(7) Å in **3**), a bond opposite to the substituents, is apparently smaller than those of the other two bonds (1.509(7) and 1.515(7) Å in **1**, 1.512(8) and 1.510(9) Å (**2**), 1.509(6)–1.525(6) Å (**3**)) while the two bond angles involving the 'back' ring bond (61.1(3) and 60.6(3)° (**1**), 60.9(4) and 61.0(4)° (**2**), 60.5(3)–61.6(3)° (**3**)) are significantly larger than those of the other one, C(9)–C(8)–C(10) (58.4(3)° (**1**), 58.1(4)° (**2**), 58.0(3) and 58.1(3)° (**3**)). This ring asymmetry is in sharp contrast with symmetrical unsubstituted cyclopropane (gas; 1.513 Å and 60° [12]), but is a rather common feature for substituted cyclopropanes [10]; it has been predicted that the 'back' ring bond is shortened for π-acceptor substituents involving C=O and N=C groups at C(8) while it is lengthened for electron donor substituents such as Cl and F [11b]. The ACC ethyl ester–Pt(II) complex [10] is of interest in that the three bond lengths (and the three bond angles) of ACC are essentially equal (averaged 'back' ring bond length from the two independent molecules = 1.50(1) Å and the other two averaged bond lengths = 1.499(8) and 1.505(8) Å; the averaged bond angles = 59.9(4), 59.9(4), 60.3(4)°). Further X-ray investigations will, therefore, be useful to elucidate which factor(s) affects the molecular dimensions of the cyclopropane ring of ACC.

Comparison of the three PLP–amino acid–metal Schiff base complexes [4b, i]

The PLP complex **3** is only the third crystal structure of a metal–PLP complex; the other two are aqua[*N*-(5′-phosphopyridoxylidene)phenylalaninato]copper(II) [4b] and aqua[*N*-(5′-phosphopyridoxylidene)glycinato]copper(II) [4i]. Characteristic structural features common to the three structures, which are all copper(II) complexes, are: (i) square-pyramidal coordination sites occupied by the tetradentate Schiff base through the same donors and by a water ligand, (ii) polymeric structure due to the axial phosphate–metal bonding, (iii) the ring nitrogen N(1) protonated and the phosphate group monovalently deprotonated, and (iv) inter-polymer N(1)–H...O(phosphate) hydrogen bonding, and additionally at least for the present and glycinato [4i] complexes, O(phosphate)–H...O(carboxylato) and O(water ligand)–H...O(phosphate) hydrogen bonds (no atomic coordinates for the phenylalaninato complex [4b] have been reported).

Model for a N-(pyridoxylidene)-1-aminocyclopropanecarboxylate Schiff base reaction intermediate in ethylene biosynthesis

Dunathan has presented a hypothesis that the bond to be cleaved around the Cα atom of the Schiff base must be orthogonal to the pyridoxal–imine plane of the extended π system to optimize π–π overlap [3]. During the process of the ACC synthesis by ACC synthase no decarboxylation occurs [5]. This suggests that the ACC carboxylate group in the Schiff base adopts an in-plane configuration and thus the Schiff base is simply hydrolyzed to give ACC. The present complexes in which the carboxylate group lies in the pyridoxal–imine plane, therefore, serve as a model for a Schiff base derived from pyridoxal and 1-aminocyclopropanecarboxylate, a reaction intermediate in the ACC biosynthesis, where, we suggest, a metal ion is replaced by a proton.

Supplementary material

Listings of hydrogen bonds and other short contacts, the thermal parameters for the non-hydrogen atoms, hydrogen atom coordinates, bond lengths and angles involving hydrogen atoms, least-squares planes, and observed and calculated structure factors are available from K. A. on request.

Acknowledgement

The authors wish to express their thanks to the Tsumura Inc. for financial support of this study.

References

1 K. Aoki and H. Yamazaki, *J. Am. Chem. Soc., 107* (1985) 6242.

2 D. E. Metzler, *Adv. Enzymol. Relat. Areas Mol. Biol., 50* (1979) 1.

3 H. Dunathan, *Adv. Enzymol. Relat. Areas Mol. Biol., 35* (1971) 79.

4 (a) E. Willstadter, T. A. Hamor and J. L. Hoard, *J. Am. Chem. Soc., 85* (1963) 1205; (b) G. A. Bentley, J. M. Waters and T. N. Waters, *Chem. Commun.*, (1968) 988; (c) S. Capasso, F. Giordano, C. Mattia, L. Mazzarella and A. Ripamonti, *J. Chem. Soc., Dalton Trans.*, (1974) 2228; (d) K. Aoki and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, (1980) 363; (e) G. J. Long, J. T. Wrobleski, R. V. Thundathil, D. M. Sparlin and E. O. Schelemper, *J. Am. Chem. Soc., 102* (1980) 6040; (f) H. M. Dawes, J. M. Waters and T. N. Waters, *Inorg. Chim. Acta, 66* (1982) 29; (g) H. M. Dawes and T. N. Waters, *J. Chem. Soc., Chem. Commun.*, (1982) 1390; (h) K. Aoki and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, (1984) 410; (i) S. P. S. Rao, H. Manohar and R. Bau, *J. Chem. Soc., Dalton Trans.*, (1985) 2051; (j) T. Ishida, K. Hatta, S. Yamashita, M. Doi and M. Inoue, *Chem. Pharm. Bull., 34* (1986) 3553.

5 H. Imaseki, in N. Takahashi (ed.), *Chemistry of Plant Hormones*, CRC Press, Boca Raton FL, 1986, pp. 249–264.

6 K. Aoki and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, (1987) 1241.

7 (a) A. N. Barrett and R. A. Palmer, *Acta Crystallogr., Sect. B, 25* (1969) 688; (b) T. Fujiwara, *Bull. Chem. Soc. Jpn., 46* (1973) 863.

8 P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M. M. Woolfson, *MULTAN78*, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, Universities of York, U.K. and Louvain, Belgium, 1978.

9 (a) A. Mosset, F. Nepveu-Juras, R. Haran and J.-J. Bonnet, *J. Inorg. Nucl. Chem., 40* (1978) 1259; (b) V. K. Sabirov, Y. T. Struchkov, A. S. Batsanov and M. A. Azizov, *Koord. Khim., 8* (1982) 1623; (c) V. K. Sabirov, A. S. Batsanov, Y. T. Struchkov and M. A. Azizov, *Koord. Khim., 9* (1983) 1701.

10 H. Wanjek, U. Nagel and W. Beck, *Chem. Ber., 118* (1985) 3258.

11 (a) M. A. M. Meester, H. Schenk and C. H. MacGillavry, *Acta Crystallogr., Sect. B., 27* (1971) 630; (b) F. H. Allen, *Acta Crystallogr., Sect. B, 36* (1980) 81.

12 S. Yamamoto, M. Nakata, T. Fukuyama and K. Kuchitsu, *J. Phys. Chem., 89* (1985) 3298.