Crystal Structure of the 1-Aminocyclopropanecarboxylate–Pyridoxal Schiff Base Complex of Copper(II): A Model for a Schiff Base Intermediate in Ethylene Biosynthesis

Katsuyuki Aoki* and Hiroshi Yamazaki

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

X-Ray structural analysis of the copper(II) complex of the Schiff base formed between 1-aminocyclopropanecarboxylate, a precursor of the plant hormone ethylene, and pyridoxal, $[Cu(C_{12}H_{13}N_2O_4)]\cdot(NO_3)\cdot H_2O$, shows that the copper atom is square-pyramidally co-ordinated by the tetradentate Schiff base, the equatorial plane being defined by the imino nitrogen, the phenolic and the carboxylate oxygens, and a water molecule, and the axial position being occupied by the hydroxymethyl oxygen of a neighbouring molecule, thus forming a one-dimensional polymer.

Pyridoxal phosphate (the cofactor form of vitamin B_6)-dependent enzymes catalyse a variety of metabolic reactions of amino acids such as decarboxylation, transamination, racemization, or C–C cleavage. Many of these reactions can also be duplicated by metal ions in the presence of pyridoxal with similar mechanisms, where the metal ion could act as a trap of the pyridoxal–amino acid Schiff base intermediate, and also exert its electronic effects to promote the subsequent reactions.[1] Despite the importance of the stereochemistry of the C_α atom in the amino acid residue in controlling the activity of the Schiff base,[2] however, only a limited number of crystal structures of metal–Schiff base complexes are available.[3] As a

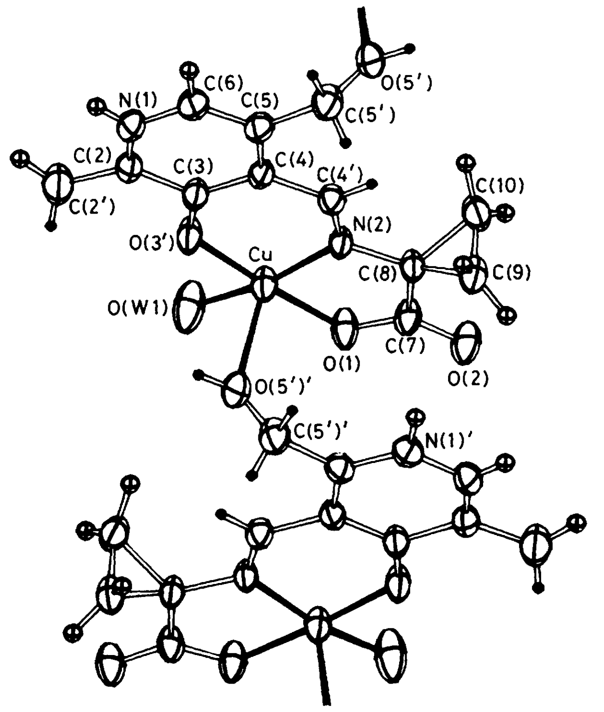

Figure 1. A segment of the polymeric [Cu(pyridoxylidene-1-aminocyclopropanecarboxylato)(H_2O)]$_n^{n+}$ structure.

continuation of our *X*-ray investigations,[3d,h] we report here the crystal structure of the copper(II) complex formed between 1-aminocyclopropanecarboxylic acid (ACC) and pyridoxal. ACC, a rare amino acid, is well known as a precursor of the plant hormone ethylene and is biosynthesized from (*S*)-adenosylmethionine by pyridoxal phosphate-dependent syntase (ACC syntase), *via* formation of the pyridoxylidene-1-aminocyclopropanecarboxylate Schiff base intermediate.[4] The present complex serves as a model for such a reaction intermediate, in accordance with Dunathan's hypothesis,[2] and gives, for the first time, the structural dimensions of the ACC molecule.

The complex was prepared from 1-aminocyclopropanecarboxylic acid, $Cu(NO_3)_2 \cdot 3H_2O$, and pyridoxal·HCl in aqueous solution (1 : 1 : 1; 0.1 mmol) at pH *ca.* 4, and its crystal structure determined.†

Figure 1 shows a segment of the cationic polymeric structure of the complex, where the pyridoxal group 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, co-ordinates to the square-pyramidal copper atom through the carboxylate O(1) [1.944(4) Å] and the phenolate O(3') [1.884(4) Å] oxygens and the imino nitrogen N(2) [1.948(5) Å], as do other known metal complexes of pyridoxal–amino acid Schiff bases, and the fourth basal donor is a water molecule [1.971(5) Å]; the axial position is occupied by the hydroxymethyl oxygen O(5') [2.358(4) Å] from a neighbouring molecule, thus creating a one-dimensional polymer. The ligation through the hydroxymethyl oxygen is not generally unusual but it is very rare for pyridoxal with only one[3f] example known, whereas for pyridoxine[5] 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)] group and the α-carbon atom C(8) are almost in the square plane [O(1), N(2), O(3'), and O(W1)] from which the metal atom deviates only slightly [0.130(2) Å towards the axial O(5')]; the carboxylate group is also nearly in this plane with the N(2)–C(8)–C(7)–O(1) torsion angle being 4.3(7)°. 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,[6] C(9)–C(10) [1.472(7) Å], a bond opposite to the substituents, is apparently (2.8σ) smaller than those of the other two bonds [1.503(8) and 1.517(7) Å], while the two bond angles involving the 'back' ring bond [61.3(3) and 60.3(3)°] are significantly (4.8σ) larger than that of the other one, C(9)–C(8)–C(10) [58.3(3)°]. This ring asymmetry is in sharp contrast with symmetrical unsubstituted cyclopropane[7] (gas) (1.513 Å and 60°), but is a rather common feature for substituted cyclopropanes.[6] Electrostatic interaction between the carboxylate planar anion and the metal ion-bridged N(1)-protonated pyridinium ring, with a parallel arrangement [3.3 Å average spacing; closest contact of O(2) · · · N(1)' 3.286(5) Å], seems to stabilize the polymeric structure.

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† *Crystal data:* $C_{12}H_{17}CuN_3O_9$, M = 410.82, monoclinic, space group $P2_1/a$, Z = 4, a = 13.222(3), b = 10.820(2), c = 11.821(3) Å, β = 110.51(2)°, U = 1583.9(7) Å^3, D_c = 1.72 g cm^{-3}, $F(000)$ = 844, μ(Mo-K_α) = 14.33 cm^{-1} (λ = 0.71073 Å), crystal dimensions 0.130 × 0.233 × 0.508 mm. Data were measured on a Rigaku AFC-5 four-circle diffractometer using graphite monochromated Mo-K_α radiation for $3 < 2\theta < 50°$. No absorption correction was made because of a small variation in F_o (<4% from the mean) for an axial reflection (at $\chi \sim 90°$). The structure was solved by heavy-atom methods and refined by block-diagonal least-squares. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms except for four of the two water molecules were located from a difference Fourier map and refined isotropically. For 2034 unique observed reflections [$F_o > 3\sigma(F_o)$] the final R value is 0.045 (R_w = 0.046). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Centre. See Notice to Authors, Issue No. 1.