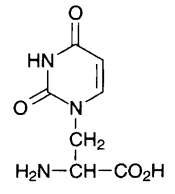
Synthesis and X-ray structure of a unique multinuclear complex constructed by a nucleobase-amino acid DL-willardiine

Mamoru Mizutani, Koichiro Jitsukawa,* Hideki Masuda* and Hisahiko Einaga

Department of Applied Chemistry, Nagoya Institute of Technology, Showa-ku, Nagoya 466, Japan

The X-ray crystal structure of a unique multinuclear complex, $[Na_2Cu_2Pd(wil)_4(H_2O)_4]$, prepared from Na_2PdCl_4, $Cu(ClO_4)_2{\cdot}6H_2O$ and DL-willardiine (wil) is determined, which reveals that the palladium atom is coordinated by the imide nitrogens of four wil ligands; two sodium ions are retained in the cavities formed by the coordinated wil molecules.

Interactions between metal ions and nucleic acids lead to an extensive range of complexes through a variety of binding modes often exploited to probe nucleic acid structure and site recognition.[1–3] With a view to constructing metal–nucleobase compounds, the crystal structures of various pyrimidine type nucleobase complexes, such as the calixarene-like complex $[\{Pt(en)(U\text{-}N^1,N^3)\}_4]$,[4,5]† the heteronuclear complex *trans*-$[Pt(NH_3)_2(1\text{-MeC})_2Pd(1\text{-MeU})]NO_3{\cdot}3H_2O$,[6] and the linear tetramer $[Pt_4(NH_3)_8(1\text{-MeU})_4][NO_3]_5{\cdot}5H_2O$,[7] have been reported and found to exhibit interesting structural features. In the course of studying metal–nucleic acid complexes, we have discovered the formation of a unique multinuclear complex containing Pd^{II}, $2Cu^{II}$ and $2Na^+$ in association with four DL-willardiine [1-(2-amino-2-carboxyethyl)uracil] molecules. Willardiine, a naturally occurring amino acid isolated from certain plants and known to be a specific and relatively potent agonist,[8–12] has three coordination sites, amino nitrogen, carboxyl oxygen of the aminoacidate chelate and imide nitrogen of the uracil residue.



DL-Willardiine (wil)

Addition of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.25 g, 0.68 mmol) to an aqueous solution (30 ml) of DL-wil (0.30 g, 1.4 mmol) at pH 7 (NaOH) quantitatively gave a neutral complex $[Cu(wil)_2]$, which was identified by its absorption spectrum (λ_{max} = 669 nm), elemental analysis (Calc. for $C_{14}H_{16}CuN_6O_8{\cdot}4H_2O$, C, 31.43; H, 4.42; N, 15.86. Found, C, 31.62; H, 4.55; N, 15.80%), and positive-ion FAB-MS {m/z = 460, $[Cu(wil)_2 + H]^+$}. To an aqueous solution containing $[Cu(wil)_2]$ (0.30 g, 0.67 mmol) was added Na_2PdCl_4 (0.20 g, 0.67 mmol) neutralized with Na_2CO_3 and a blue precipitate of $[Na_2Cu_2Pd(wil)_4(H_2O)_4]$ **1** was quantitatively obtained (Calc. for $C_{28}H_{28}Cu_2N_{12}Na_2O_{16}Pd{\cdot}10H_2O$, C, 26.94; H, 3.88; N, 13.47. Found, C, 26.66; H, 3.56; N, 13.15%). Single crystals of complex **1** suitable for X-ray analysis were obtained from an aqueous solution after several weeks.

The structure determination shows that complex **1** has the formula $[Na_2Cu_2Pd(wil)_4(H_2O)_4]{\cdot}9H_2O$, consisting of a palladium, two copper, and two sodium ions, four wil ligands and four water molecules (Fig. 1).‡ Each copper atom is coordinated by D- and L-wil ligands *cis* to each other equatorially and by one water molecule in an apical position. The palladium atom is coordinated in a square-planar geometry by four uracil moieties of the wil molecules also coordinating to copper. Each sodium ion completes an octahedral geometry by coordinating to four uracil carbonyl oxygens and one water molecule; a short Pd···Na interaction completes the coordination. The sodium atoms, Na(1) and Na(2), are displaced by 0.81 and 0.82 Å out of the plane defined by the four uracil carbonyl oxygen atoms toward the water oxygen atoms, O(1W) and O(2W), respectively.

Tetrakis(nucleobase) palladium complexes are rare and only one previous X-ray crystal structure of this type, $[Pd(1\text{-MeC-}N^3)_4][NO_3]_2{\cdot}2H_2O$, has been previously reported.[13] The Pd–N bond lengths in **1** [2.034(9), 2.027(9), 2.040(9) and 2.023(9) Å] are comparable to those for previously reported palladium complexes with pyrimidine nucleobases; 2.056(3) and 2.031(3) Å in $[(bpy)Pd(1\text{-MeT})_2Pd(bpy)][NO_3]_2{\cdot}5.5H_2O$,[14] 2.072(5) Å in $[Pd(gly\text{-}L\text{-}hisN^{\alpha},O)(1\text{-MeC})]{\cdot}3.5H_2O$,[15] 2.056(4) Å in *trans*-

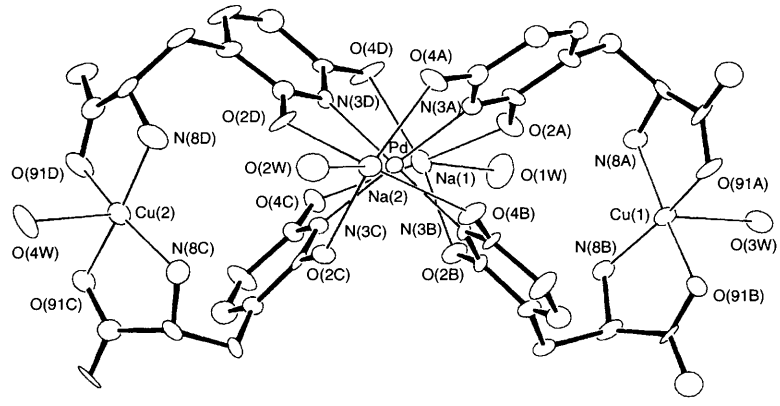


Fig. 1 ORTEP representation of the $[Na_2Cu_2Pd(wil)_4(H_2O)_4]$ **1**. Important interatomic distances (Å) and angles (°): Pd–Na(1) 3.003(5), Pd–Na(2) 2.950(5), Pd–N(3A) 2.034(9), Pd–N(3B) 2.027(9), Pd–N(3C) 2.040(9), Pd–N(3D) 2.023(9), Na(1)–O(2A) 2.245(9), Na(1)–O(2B) 2.385(9), Na(1)–O(4C) 2.310(9), Na(1)–O(4D) 2.357(10), Na(2)–O(4A) 2.359(9), Na(2)–O(4B) 2.311(10), Na(2)–O(2C) 2.432(9), Na(2)–O(2D) 2.271(9); N(3A)–Pd–N(3B) 88.1(4), N(3B)–Pd–N(3C) 90.5(3), N(3C)–Pd–N(3D) 89.2(3), N(3D)–Pd–N(3A) 92.3(4).

$[(NH_3)_2Pt(1\text{-}MeC)_2Pd(1\text{-}MeU)]NO_3{\cdot}3H_2O$,[6] and 2.046(7), 2.035(7), 2.037(7) and 2.040(7) Å in $[Pd(1\text{-}MeC\text{-}N^3)_4][NO_3]_2{\cdot}2H_2O$.[13]

The short Pd···Na distances in **1** of 3.003(5) and 2.950(5) Å, may be explained in terms of charge neutralization of the Pd^{II} ion due to the tetrakis-coordination of the deprotonated imide nitrogens. The binding energy of the palladium atom in **1** as measured by XPS (C 1s = 285.0 eV) indicated that it has a neutral or slightly negative charge ($3d_{3/2}$ = 339.4 eV, $3d_{5/2}$ = 334.2 eV), *cf.* $PdCl_2$ ($3d_{3/2}$ = 343.5 eV, $3d_{5/2}$ = 338.2 eV), Pd ($3d_{3/2}$ = 340.3 eV, $3d_{5/2}$ = 335.0 eV).

Presumably the sodium cations are captured into the cavities constructed by the assembly of four carbonyl oxygens of the tetrakis(uracilato)palladium and the slightly negatively charged palladium atom. Detailed examination of the interactions between sodium and palladium, as indicated by the significantly short distances, is now in progress.

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Footnotes

† *Abbreviations*: wil = willardiine, 1-MeU = deprotonated form of 1-methyluracil; 1-MeT = deprotonated form of 1-methylthymine; 1-MeC = deprotonated form of 1-methylcytosine; 1-MeC-N^3 = deprotonated form (at N^3) of 1-methylcytosine; U, monodeprotonated form of uracil.

‡ *Crystal data for* **1**: $(C_{28}H_{28}Cu_2N_{12}Na_2O_{16}Pd){\cdot}13H_2O$, M = 1302.29, orthorhombic, space group *Pbca*, a = 20.893(2), b = 17.522(1), c = 25.758(2) Å, Z = 8, U = 9795.8 Å^3, D_c = 1.766 g cm^{-3}, μ(Cu-Kα) = 50.86 cm^{-1}, $F(000)$ = 5312. A total of 9097 unique reflections were collected on an Enraf-Nonius CAD4-Express four-circle diffractometer. A total number of 4195 reflections with $I > 3\sigma(I_o)$ were used in the structure analysis and refinement using the SDP-MolEN program system. Absorption correction was applied by the ψ-scan method. Final R and R_w factors were 0.064 and 0.075, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/85.

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