Formation of a Novel Diaqua Disodium Tetrakis(1-methyluracilato)palladium Complex with a Unique Supramolecular Channel Structure

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(Received April 10, 1998; CL-980266)

A novel $[Na_2Pd(1\text{-}MeU^-)_4(H_2O)_2]_n$ (**1**) columnar complex is prepared from the reaction of an aqueous solution containing Na_2PdCl_4 with four equivalent amount of 1-methyluracil (1-MeUH) in the presence of Na_2CO_3. X-ray structure of **1** reveals that the complex forms an infinite supramolecular channel structure in the crystal.

Nature uses weak intermolecular forces such as hydrogen bonding, hydrophobic and electrostatic interactions to form self-assembled structures such as DNA and proteins. Nucleic acid/nucleobase-metal interactions also form unique self-assembled metal complexes through a variety of binding modes, which are often employed to probe nucleic acid structures and their site-specific recognition.[1-4] Such a metal ion-directed self-assembly leads to construction of supramolecular structures such as helicates,[5,6] grids,[7,8] rings,[9] and cages.[10] Here, we report on a novel infinite columnar structure of $[Na_2Pd(1\text{-}MeU^-)_4(H_2O)_2]_n$, which forms a supramolecular channel structure constructed by self-assembling.

Diaqua disodium tetrakis(1-methyluracilato)palladium complex (**1**) was prepared in an aqueous solution containing Na_2PdCl_4 and 4 equivalent amount of 1-methyluracil (1-MeUH) in the presence of Na_2CO_3 at pH 9~10. The elemental analysis of crystal **1** (C, 36.80; H, 3.10; N, 17.11) was in good accord with the values calculated for $Na_2PdC_{20}H_{20}N_8O_8$ (C, 36.80; H, 3.09; N, 17.16).

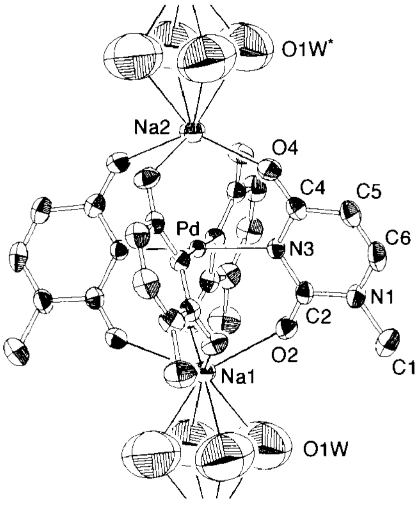

Figure 1. Crystal structure of $[Na_2Pd(1\text{-}MeU^-)_4(H_2O)_2]_n$ (**1**) showing the atom numbering scheme. Selected bond lengths (Å): Pd-N(3) 2.037(3), Na(1)-O(1W) 2.445(8), Na(1)-O(2) 2.400(3), Na(2)-O(1W*) 2.504(8), Na(2)-O(4) 2.419(3), N(1)-C(1) 1.453(7). The atom with asterisk is related to the non-asterisk atom.

A pale-yellow crystal of **1** was subjected to a single X-ray diffraction measurement.[11] The complex **1** crystallizes in the tetragonal system with space group *P4/n*, which contains four sodium cations, two $[Pd(1\text{-}MeU^-)_4]^{2-}$ anions and twenty-two water molecules in the unit cell. The number of waters of crystallization are 2.75 molecules as an asymmetric unit, the occupations of which were determined by refinement of the population. The waters coordinating to a sodium ion (Figure 1) are located as disordered molecules with the occupation of 0.5 around a crystallographic four-fold axis, that with the occupation of 0.25 lies on another four-fold axis, and the other two molecules fill the crystalline spaces. These water molecules are weakly bound by hydrogen bonds each other.

As shown in Figure 1, the Na···Pd···Na atoms lie on the required four-fold axis, and the palladium atom is coordinated with four N3-deprotonated imide groups of four uracil rings (Pd - N(3) = 2.037(3) Å) in square-planar geometry, whose overall structure is characterized as a head-head-head-head propeller-like one; the mean dihedral angle between the palladium coordination plane and uracil rings is 71.4°. Remarkably, the axial positions of the palladium atom are occupied by two sodium ions, each of which is surrounded with four uracil carbonyl oxygens (Na(1) - O(2) = 2.400(3), Na(2) - O(4) = 2.419(3) Å) and water molecules (Na(1) - O(1W) = 2.445(8), Na(2) - O(1W*) = 2.504(8) Å). The separations between palladium and sodium atoms, 3.007(4) and 3.137(3) Å, are brought so close for the interatomic distance between the cationic atoms, although they are comparative with the sum (2.79 Å) of the van der Waals radius of palladium atom (1.63 Å) and the ionic one of sodium atom (1.16 Å).[12] This may be reasonably explained in terms of a weak attractive interaction between the positively-charged sodium atom and the charge-neutralized palladium atom that was promoted by coordination of four deprotonated anionic $1\text{-}MeU^-$ molecules, although the bonding character between them are not clear from this study. This unique structure of **1** is also identified by positive ion FAB mass spectra giving parent peaks at m/z = 653 and 675 which are assignable to $[Na_2Pd(1\text{-}MeU^-)_4 + H]^+$ and $[Na_2Pd(1\text{-}MeU^-)_4 + Na]^+$, respectively. ^1H-NMR spectra of complex **1** in D_2O demonstrated that all protons of the $1\text{-}MeU^-$ moiety shifted to upper-field side in comparison with the corresponding peaks for metal free $1\text{-}MeU^-$ at pH 11, although the NMR peaks of ligand generally exhibit a lower-field shift by coordination of metal ion: $1\text{-}CH_3$, 5-H, and 6-H protons of metal-free $1\text{-}MeU^-$ appeared at 3.33, 5.73, and 7.48 ppm were observed at 3.25, 5.47, and 7.27 ppm by coordination of Pd(II) ion, respectively. This unique upper-field shift may be explained as follows: The electrons on the Pd atom which is donated by coordination of four electron-donating $1\text{-}MeU^-$ molecules are delocalized on the 1-MeU$^-$ ring through the back-donation to cause the upper-field shifts of the proton peaks. The extremely unique short contact between Pd and Na, which is shown in Figure 1, may be understood as an attractive interaction between the electron-rich Pd atom and Na^+ cations.

Recent publications[13-16] have given several notable examples of metal-directed multicomponent supramolecules: For example the oligocatecholate complex self-assembled by titanium and alkali metals formed a cryptand-type helicate structure. The crystal structure of **1** also demonstrates a unique characteristic as a supramolecular assembly of the $[Na_2Pd(1\text{-}MeU^-)_4(H_2O)_2]$ unit. The $[Na_2Pd(1\text{-}MeU^-)_4(H_2O)_2]$ complex, which is bridged by water molecules coordinating to each sodium ion, forms an infinite column running along the z-axis in the crystal, which contacts with the neighboring columns each other through the hydrogen bond networks (2.76 - 3.00 Å) and π-π stacking interactions (the separation distance between the uracil rings, 3.50 Å), as shown in Figure 2. The columns are constructed through the immobilization of spherical sodium ions and retention of water molecules on the sodium ions together with weak interactions between them, which play as the key factors for generating an infinite supramolecular channel including a water molecule as the guest molecule. To the best of our knowledge, the complex represents the first example of an inorganic supramolecular structure with an infinite one-dimensional channel linked by a combination of non-covalent interactions such as hydrogen bond, CH-π and π-π interactions, although the analogous Pd complexes, such as $Na_2[Pd(succinimidato)_4]$,[17] [Pt(ethylenediamine)(uracilato)]$_4^{4+}$,[18] and *trans*-$K_2[PtI_2(1\text{-}MeU)_2]\cdot 6H_2O$,[19] were previously reported.

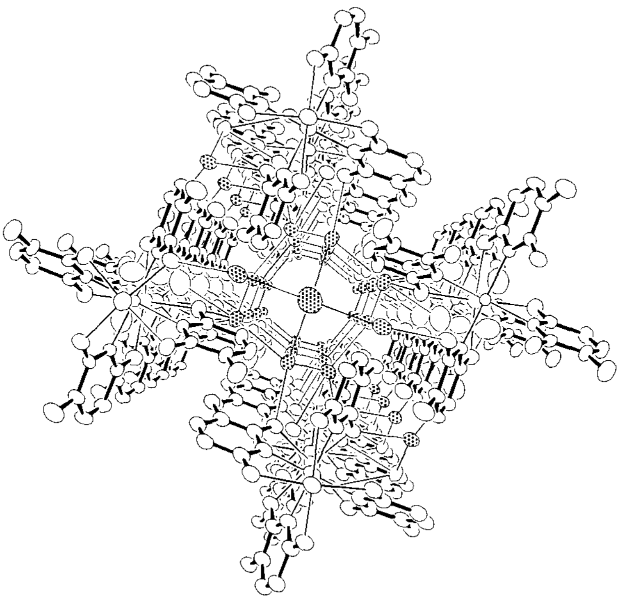

Figure 2. Perspective view along the *c* axis of the supramolecular channels in crystal **1** formed by self-assembly of $[Na_2Pd(1\text{-}MeU^-)_4(H_2O)_2]_n$ columns through hydrogen bond networks (thin lines) and π-π interactions. The water molecules are shaded.

This study was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture of Japan. We are also grateful to the Chemical Materials Centre, the Institute for Molecular Science, for assistance in obtaining the FAB mass spectra.

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11 Crystal data for **1**: $Na_2Pd(C_{20}H_{20}N_8O_8)\cdot 11H_2O$, M = 850.97, tetragonal, $P4/n$, a = 13.192(2), c = 10.186(1) Å, Z = 2, V = 1772.5(3) Å^3, D_C = 1.594 g cm^{-3}, μ(Mo Kα) = 6.35 cm^{-1}, $F(000)$ = 876.0. A total of 2069 unique reflections were collected on an Enraf Nonius CAD4-EXPRESS four-circle diffractometer, of which 1913 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 Ψ scan method. Final R and R_w factors were 0.034 and 0.038, respectively.
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