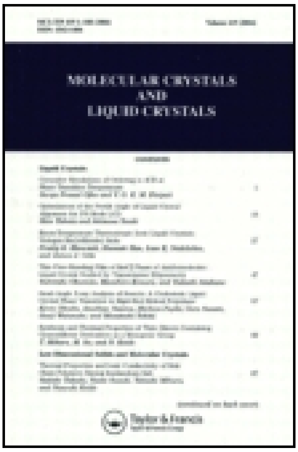

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# Three-Dimensional H-Bonded Networks Based on Mono- and Tetranuclear Metal-Pteridine Complexes

Minoru Mitsumi [a] , Jiro Toyoda [b] , Kazuhiro Nakasuji [b] , Nobuko Kanehisa [c] & Yasushi Kai [c]

[a] Department of Functional Molecular Science, The Graduate University for Advanced Studies, Myodaiji, Okazaki, 444, Japan

[b] Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka, 560, Japan

[c] Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka, 565, Japan

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# THREE-DIMENSIONAL H-BONDED NETWORKS BASED ON MONO- AND TETRANUCLEAR METAL–PTERIDINE COMPLEXES

MINORU MITSUMI,[a] JIRO TOYODA,[b] KAZUHIRO NAKASUJI,*,[b]
NOBUKO KANEHISA,[c] and YASUSHI KAI[c]

[a]Department of Functional Molecular Science, The Graduate University for Advanced Studies, Myodaiji, Okazaki 444, Japan

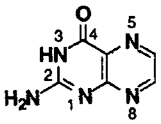
[b]Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

[c]Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

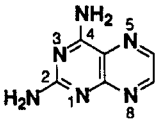
Abstract The crystal structure of the transition metal–pteridine complexes having three-dimensional hydrogen-bonded (H-bonded) network and stacking interactions between pteridine ligands are described; (1) Mononuclear copper(II)–pteridine complex and (2) Tetranuclear palladium(II)–pteridine complex.

## INTRODUCTION

Control of the cooperative interaction between electron-transfer and proton-transfer in hydrogen-bonded charge-transfer (HBCT) systems is a new way to regulate electronic properties in the solid state.[1,2] In principle, CT interaction can be related to the redox properties of the metal atoms and/or the stacking interactions between the ligands. In order to study the basic chemistry of such systems, we need to construct metallosupramolecular systems in which ligands are connected by intermolecular H-bonds. As a basic skeleton of the ligands, we have utilized the pteridine derivatives, such as pterin (HPR) and 2,4-diaminopteridine (DAP), which have the ability to chelate to metal atoms and H-bonding sites of NH···O and NH···N types in the solid state. Pteridine–metal complexes have recently been studied to mimic both the metal environment and reactivity of the metal site of the enzymes and some of these have been characterized by X-ray crystallography.[3,4] We now report the crystal structures



**HPR**



**DAP**

of mono- and tetranuclear transition metal complexes having three-dimensional H-bonded network and stacking interaction based on pteridine ligands, $[Cu(PR)_2(H_2O)_2]\cdot 2H_2O$ (**1**) and $[\{PdCl(DAP)\}_4]Cl_4\cdot 4EtOH\cdot 4H_2O$ (**2**).

## CRYSTAL DATA

The Crystallographic Data for **1** and **2** are summarized in Table I.

TABLE I Crystallographic Data for **1** and **2**.

| | **1** | **2** |
|---|---|---|
| chem formula | $C_{12}H_{16}CuN_{10}O_6$ | $C_{32}H_{56}Cl_8N_{24}O_8Pd_4$ |
| fw | 459.87 | 1614.26 |
| space group | $P\bar{1}$ | $I4_1/a$ |
| $a$, Å | 7.812(2) | 21.358(2) |
| $b$, Å | 8.598(3) | 17.387(5) |
| $c$, Å | 6.863(2) | |
| $\alpha$, deg | 108.32(2) | |
| $\beta$, deg | 95.56(2) | |
| $\gamma$, deg | 74.84(2) | |
| $V$, Å$^3$ | 422.3(2) | 7930(2) |
| $Z$ | 1 | 4 |
| $\rho_{calc}$, g·cm$^{-1}$ | 1.808 | 1.352 |
| $T$, K | 296 | 296 |
| $\lambda$, Å | 0.71069 | 0.71069 |
| $\mu$, cm$^{-1}$ | 13.54 | 12.11 |
| $R^a$ | 0.033 | 0.085 |
| $R_w{}^b$ | 0.026 | 0.095 |

[a] $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $R_w = \{(\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2)\}^{1/2}$.

### (1) Mononuclear Copper(II)–Pteridine Complex 1.

Single crystals of **1** were obtained at room temperature by diffusion method in an H-shaped tube containing an aqueous solution of $Cu(ClO_4)_2\cdot 6H_2O$, an aqueous solution of HPR and NaOH, and water. The complex possesses an inversion center (Figure 1).

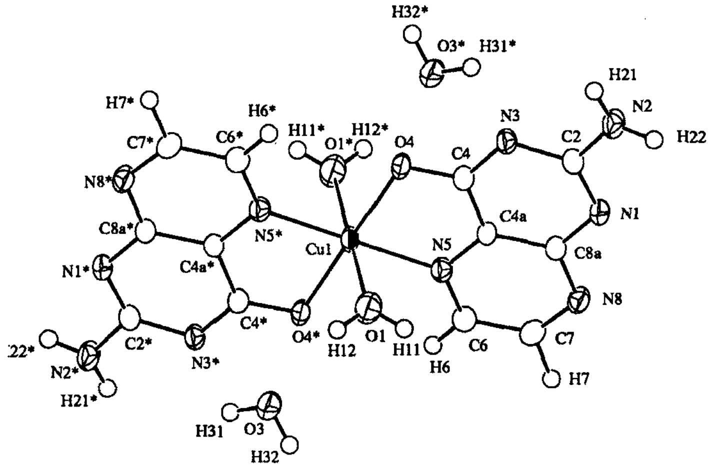


FIGURE 1 ORTEP diagram for **1** with atomic numbering scheme and 50 % thermal ellipsoids. Selected bond lengths (Å) are as follows: Cu(1)–O(1), 2.407(2); Cu(1)–O(4), 1.971(2); Cu(1)–N(5), 2.025(2). Selected bond angles (deg) are as follows: O(1)–Cu(1)–O(4), 87.82(8); O(1)–Cu(1)–O(4*), 92.18(8); O(1)–Cu(1)–N(5), 87.67(9); O(1)–Cu(1)–N(5*), 92.33(9); O(4)–Cu(1)–N(5), 84.23(8); O(4)–Cu(1)–N(5*), 95.77(8).

The coordination sphere of copper(1) atom has an elongated octahedral coordination geometry defined by two N(5) atoms and two O(4) atoms of PR ligands lying in the equatorial plane and by two water molecules at apexes. The dihedral angle between the plane formed by O(4), Cu(1), and N(5) atoms and the ligand PR' plane is 13.11° and the Cu(1) atom deviates by 0.356 Å from the plane of the ligand PR. Packing diagrams of **1** is presented in Figure 2. H-bonding distances and angles are given in Table II.[5] In **1**, the noncoordinated water molecules are involved in a three-dimensional H-bonded network. The molecular units of **1** are linked into a two-dimensional molecular sheet parallel to the *ab* plane via H-bonds among PR, coordinated and noncoordinated water molecules (*a* direction: O(1)–H(12)···O(3)$^b$ and O(3)–H(32)···O(4)$^d$, *b* direction: O(1)–H(11)···N(8),$^a$ N(2)–H(22)···O(3),$^f$ and O(3)–H(31)···N(1)$^c$). The molecular sheets are further linked to each other through double H-bonds of N(2)–H(21)···N(3)$^e$ between molecular units related by a center of inversion in position [0.5, 0.5, 0.5] to form a three-dimensional H-bonded network. In the sheet, there are two types of PR stacking along the *a*-axis with the alternated distances of 3.25 and 3.20 Å, respectively.

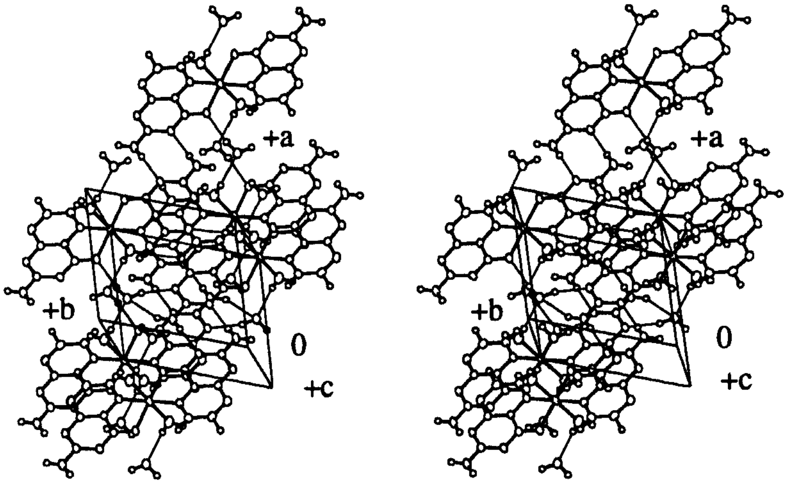


FIGURE 2 Stereoscopic ORTEP pair of **1** showing three-dimensional H-bonded network and pteridine stacking interaction.

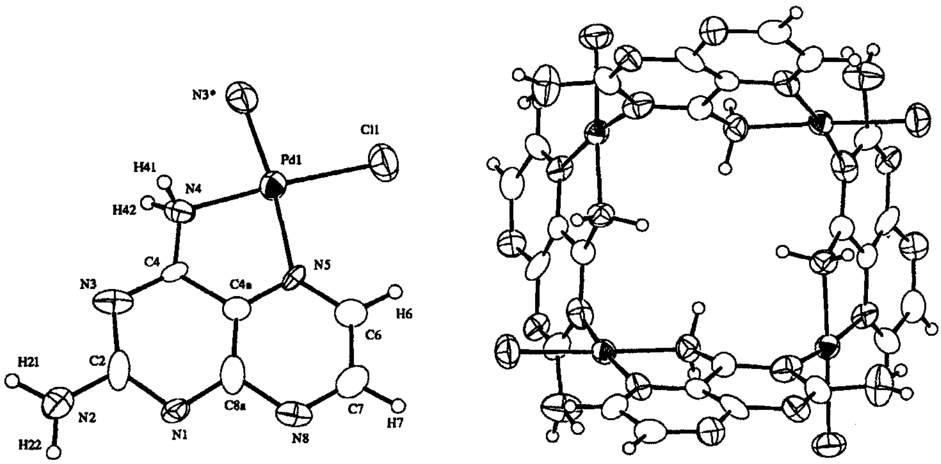
TABLE II H-Bonding Distances and Angles for **1**.

| D–H···A | D–H Å | H···A Å | D···A Å | D–H···A angle, deg |
|---|---|---|---|---|
| O(1)–H(11)···N(8)[a] | 0.826(2) | 2.135(2) | 2.953(3) | 170.5(2) |
| O(1)–H(12)···O(3)[b] | 0.907(2) | 2.031(2) | 2.823(3) | 145.2(2) |
| O(3)–H(31)···N(1)[c] | 0.912(2) | 1.966(2) | 2.840(3) | 159.9(1) |
| O(3)–H(32)···O(4)[d] | 0.888(2) | 1.994(2) | 2.867(3) | 167.4(2) |
| N(2)–H(21)···N(3)[e] | 0.903(3) | 2.092(2) | 2.987(3) | 170.5(2) |
| N(2)–H(22)···O(3)[f] | 0.889(2) | 2.303(2) | 3.053(3) | 142.1(2) |

Symmetry operations: [a] $-x, 1-y, -z$; [b] $x, y, z$; [c] $1+x, -1+y, z$; [d] $1+x, y, z$; [e] $-1-x, 1-y, 1-z$; [f] $-1+x, 1+y, z$.

### (2) Tetranuclear Palladium(II)–Pteridine Complex 2.

The crystals of **2** were obtained from dimethyl sulfoxide–ethanol solution. The ORTEP diagrams for $[PdCl(DAP)]^+$ monomeric unit and tetranuclear cation are shown in Figure 3.



(a)

(b)

FIGURE 3 (a) ORTEP diagram for monomeric unit in cation in **2** with atomic numbering scheme and 30 % thermal ellipsoids. (b) ORTEP diagram for tetranuclear cation in **2** with 30 % thermal ellipsoids. Selected bond lengths (Å) are as follows: Pd(1)–Cl(1), 2.298(8); Pd(1)–N(3*), 1.95(3); Pd(1)–N(4), 1.95(2); Pd(1)–N(5), 1.97(2). Selected bond angles (deg) are as follows: Cl(1)–Pd(1)–N(3*), 91.1(7); Cl(1)–Pd(1)–N(5), 95.2(7); N(3*)–Pd(1)–N(4), 91.4(9); N(4)–Pd(1)–N(5), 82.2(9).

The chloride ions and ethanol and water molecules have been omitted for clarity; these ions and molecules are disordered. The Pd(1) atom in monomeric unit is surrounded by N(5) atom, amino nitrogen N(4) at C(4) of DAP, and chloride ion. The remaining site is occupied by N(3*) atom of the nearest neighboring DAP, and thus the $[PdCl(DAP)]^+$ units form the cyclic tetranuclear structure. This type of cyclic tetranuclear systems were reported by Lippert et al. and Ito et al. using uracil derivatives.[8] Each monomeric units in the tetranuclear cation are related to the crystallographic $\bar{4}$ axis perpendicular to the $Pd_4$ plane. The central part of the tetranuclear cation is filled by the hydrogen atoms of amino groups at C(2). The N(2)···N(2) separations are 3.60(3) Å (neighboring) and 5.06(3) Å (diagonal), respectively. The dihedral angle between the Pd plane and DAP plane is 85.3°. The Pd···Pd separations are 5.166(3) Å (neighboring) and 7.034(4) Å (diagonal), respectively. The stereoviews of the unit cell are shown in Figures 4 and 5. As evident from Figure 4, the DAP ligands of adjacent cations are stacked (the mean stacking distance is 3.38 Å) and the adjacent cations are connected via double

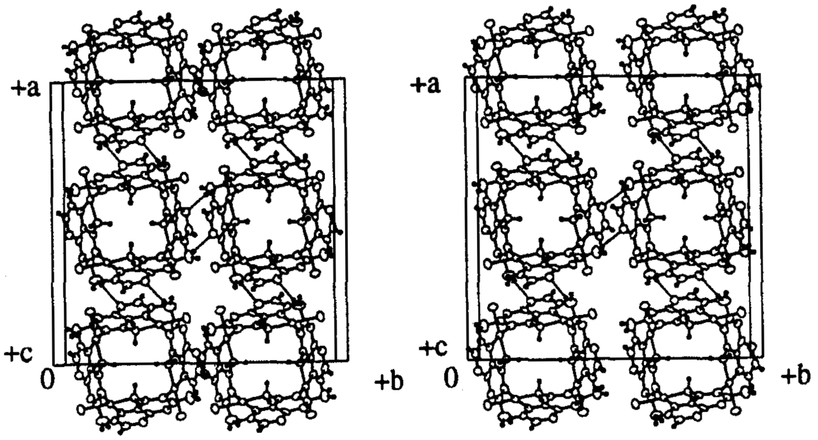


FIGURE 4 Stereoscopic ORTEP pair of **2** showing the three-dimensional H-bonded network and pteridine stacking interactions. The view is along the *c*-axis.

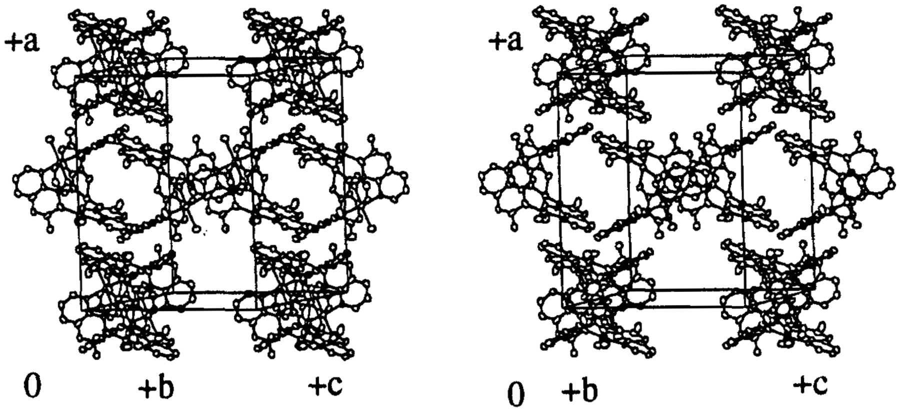


FIGURE 5 Stereoscopic ORTEP pair of **2** showing the channels along *a*- and *b*-axes.

intermolecular H-bonds; N(2)···N(8) = 3.30(3) Å. The resulting arrangement of cations produces the channels parallel to the *a*- and the *b*-axis (see Figure 5).

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