# Articles

## Structure of a Copper(II) Hexaazamacrotricyclic Complex: (1,3,6,9,11,14-Hexaazatricyclo[12.2.1.1$^{6,9}$]octadecane)-copper(II) Perchlorate

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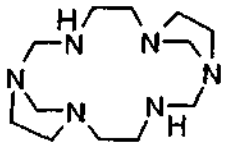
The crystal structure of (1,3,6,9,11,14-hexaazatricyclo[12.2.1.1$^{6,9}$]octadecane)copper(II) perchlorate, $Cu(C_{12}H_{26}N_6)(ClO_4)_2$, has been determined by the X-ray diffraction methods. The crystal data are as follows: $Mr=516.9$, triclinic, $a=8.572$ (2), $b=8.499$ (3), $c=15.204$ (3) Å, $\alpha=80.42$ (5), $\beta=73.57$ (3), $\gamma=69.82$ (4)°, $V=994.2$ Å$^3$, $D_c=1.726$ gcm$^{-3}$, space group P$\bar{1}$, $Z=2$, $\mu=21.27$ cm$^{-1}$, $F(000)=534$ and $T=297$ K. The structure was solved by direct methods and refined by full-matrix least-squares methods to an $R$ value of 0.081 for 1608 observed reflections measured with graphite-monochromated Mo Kα radiation on a diffractometer. There are two independent complexes in the unit cell. The two copper ions lie at the special positions (1/2, 0, 0) and (0, 1/2, 1/2) and each complex possesses crystallographic center of symmetry. Each Cu ion is coordinated to four nitrogen donors of the hexaazamacrotricyclic ligand and weakly interacts with two oxygen atoms of the perchlorate ions to form a tetragonally distorted octahedral coordination geometry. The Cu-N (*sec*), Cu-N (*tert*) and Cu-O coordination distances are 1.985 (14), 2.055 (14) and 2.757 (13) Å for the complex A and 1.996 (10), 2.040 (11) and 2.660 (13) Å for the complex B, respectively. The macrocycles in the two independent cations assume a similar conformation with the average *r.m.s.* deviation of 0.073 Å. Two 1,3-diazacyclopentane ring moieties of the hexaazamacrotricyclic ligand are placed oppositely and almost perpendicularly to the square coordination plane of the ruffled 14-membered macrocycle. The secondary N atoms are hydrogen-bonded to the perchlorate O atoms with distances of 3.017 (23) and 3.025 (19) Å for the complexes A and B, respectively.

### Introduction

Macrocyclic complexes show enhanced thermodynamic and kinetic stabilities and the characteristic properties inaccessible to the complexes with non-cyclic chelate ligands. The macrocyclic complexes are often prepared by the metal template reactions because they provide selective and high yielding routes to the complexes of new ligands. Recently the facility of template syntheses involving formaldehyde and amines to yield complexes of multidentate and macrocyclic ligands has been demonstrated[1-8]. In these reactions, formaldehyde links two amine moieties in the cyclization to yield methylenediamine ($NCH_2N$) linkages.



L

The Ni(II) and Cu(II) complexes of the hexaazamacrotricyclic ligand 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1$^{6,9}$]octadecane, (L), have been synthesized from the simple template condensation reactions of diethylenetriamine with formaldehyde in the presence of the metal ion[6,7]. The macrotricyclic ligand L is quite interesting because it is a fully saturated hexaazamacrocycle acting as a tetradentate ligand. Furthermore, the ligand contains 1,3-diazacyclopentane ring moieties fused to the 14-membered macrocycles. The crystal structures of four-coordinate $[Ni(L)]Cl_2\cdot H_2O$[6] and five-coordinate $[Cu(L)Cl]ClO_4$[9] were previously determined. Here we report the crystal structure of six-coordinate $[Cu(L)(ClO_4)_2]$.

### Experimental

Title complex was synthesized by the template condensation reaction of diethylenetriamine and formaldehyde in the presence of $Cu(OAc)_2\cdot H_2O$, followed by addition of $LiClO_4$[7]. Opaque red crystals were obtained by recrystallization from hot water solution. A crystal having dimensions of *ca.* 0.2 ×0.2×0.6 mm was used in the experiment. An initial X-ray photographic examination established that the crystal system was triclinic. The space group was assumed to be P$\bar{1}$ and confirmed later in the process of structure determination. The unit cell parameters were refined by a least-squares fit of 2θ angles for 22 reflections (5.6°<2θ<29°) measured with graphite-monochromated Mo Kα radiation on an automated Rigaku AFC diffractometer. The crystal data are as follows: $Mr=516.9$, triclinic, $a=8.572$ (2), $b=8.499$ (3), $c=15.204$ (3) Å, $\alpha=80.42$ (5), $\beta=73.57$ (3), $\gamma=69.82$ (4)°, $V=994.2$ Å$^3$, $D_c=1.726$ gcm$^{-3}$, $D_m=1.71$ gcm$^{-3}$ by floatation in ($H_2O/H_2SO_4$) solution, space group P$\bar{1}$, $Z=2$, $\mu=21.27$ cm$^{-1}$, $F(000)=534$. Reduced cell data are $a=8.572$, $b=15.196$, $c=8.590$ Å, $\alpha=91.61$, $\beta=110.18$, $\gamma=73.68$°. The intensity data were collected with Zr-filtered, graphite-monochromated Mo Kα radiation using ω-2θ scan technique over a scan range (1.4+0.3 tanθ)° in ω at a scan rate of 8°/min in 2θ. Indivi-

dual scans of many reflections showed split peaks and thus the reflections with a large background ratio were remeasured with a scan width of $(1.8+0.2\tan\theta)^\circ$ in $\omega$. The background was counted for 10 s on either side of the peak. Receiving slit with a diameter of 4.5 mm was used on the detector and the minimum count for the peak was set to 6 cps. Three standard reflections were monitored every 50 reflections throughout the data collection and showed random variations of ± 1% with no significant trends. After corrections for Lorentz and polarization effects appropriate for the graphite−monochromated ($2\theta_m=12.1^\circ$ for Mo $K\alpha$) radiation were applied, the intensity data were converted to relative structure amplitudes. Of the 3502 independent reflections ($h$ −10 to 10, $k$ −10 to 10, $l$ 0 to 18) measured within the range of $5^\circ<2\theta<50^\circ$, 1608 (45.9%) were considered to be observed as defined by $F_o>6\sigma(F_o)$. The reflections with $h+k+l=2n+1$ were generally very weak, especially in the high $2\theta$ region. This phenomenon was later found to be related to the presence of the Cu ions at the special positions. No correction for absorption and extinction effects was applied.

The structure was solved by direct methods with the program *SHELXS-86* and refined by full-matrix least-squares methods on $F$ with *SHELX-76*[10]. From the initial $E$ map calculated with the phase set having the highest reliability index, it was possible to identify the positions of all non-hydrogen atoms except one oxygen in perchlorate. After one cycle of isotropic refinement, the remaining oxygen atom was identified in the subsequent difference Fourier synthesis. Another cycle of anisotropic refinement reduced the $R$ value from 0.12 to 0.10. After anisotropic refinement using the weighting scheme, some hydrogens could be identified in the difference Fourier map, but their thermal parameters became nonpositive or their positions moved badly in further refinements. At this stage, there was an indication of disorder in the perchlorate B. Among the various disordered models tested, the rotational disorder model with the Cl-O(1B) bond as a rotational axis gave the best results. A common site occupancy factor was assigned to the three oxygen atoms in the perchlorate B. After the site occupancy factors were refined, the oxygen atoms in the major sites (*s.o.f.* of 0.861) were refined anisotropically and those in the minor sites (*s.o.f.* of 0.139) isotropically. The positional parameters of the hydrogen atoms were calculated geometrically with idealized bond length (1.08 Å) and angles and the isotropic thermal parameters were fixed with the value of 1.3 times those of the bonded atoms. The refinement converged at $R=0.081$ ($R=\Sigma||K|F_o|-|F_c||/\Sigma K|F_o|$, where $K$ is a scale factor) for 1608 observed reflections. The weighted $R$ ($R\omega=[\Sigma(\omega K|F_o|-|F_c|)^2/\Sigma\omega K|F_o|^2]^{1/2}$) factor was 0.087. The number of variables was 278. The S value (goodness of fit: $[\Sigma\omega(K|F_o|-|F_c|)^2/(N_o-N_p)]^{1/2}$ where $N_o$ is the total number of reflections and $N_p$ is the number of variables refined) is 1.63. The function $\Sigma\omega(|F_o|-|F_c|)^2$ was minimized in the refinement. $\omega$, the weight of the reflection, was defined by $k/(\sigma^2(F_o)+g(F_o)^2)$, where $\sigma(F_o)$ was from counting statistics and $k$ and $g$ were optimized in the least-squares procedure ($k=1.498$ and $g=0.00395$). The final difference Fourier map was relatively noisy. It revealed a maximum peak of 1.11 eÅ$^{-3}$ in the vicinity of the Cu ion. The height of the minimum peak was −0.69 eÅ$^{-3}$. The maximum (shift/esd) was −0.502 for the isotropic thermal parameter of O(3′) in the final refinement cycle. The $R$ and $R\omega$ values were 0.113 and 0.116, respectively, for all unique 2242 reflections. All calculations except direct methods (SHELXS-86 on an IBM-AT) were performed with *SHELX-76* on an IBM 3090. Atomic scattering factors and the terms of the anomalous-dispersion correction were from *International Tables for X-ray Crystallography*[11] as incorporated in *SHELX-76*. The final atomic coordinates and the thermal parameters are listed in Table 1*.

## Discussion

A view of one cation with the atomic numbering scheme is presented in Figure 1. A stereoscopic ORTEP[12] crystal packing diagram is shown in Figure 2. Bond distances and angles are listed in Table 2.

The asymmetric unit consists of two halves of the two independent complexes, each of which possesses crystallographic center of symmetry. Each Cu ion is coordinated to the two tertiary and the two secondary nitrogen atoms of the macrocycle in the equatorial positions and weakly interacts with the two oxygen atoms of the two perchlorate ions in the axial positions, forming a tetragonally distorted octahedral complex. The IR spectrum (Nujol mull) showed no indication for the coordination of $ClO_4^-$ anions (no splitting of $ClO_4^-$ band around 1100 cm$^{-1}$) and the UV/vis spectra ($MeNO_2$ solutions) also indicated the square-planar coordination geometry of the complex.[7] However, the present X-ray crystal structure unambiguously shows that there are interactions between Cu(II) ion and the perchlorate anions in the crystal lattice. Both complexes (designated A and B) assume a similar conformation, though not exactly the same. Two 1,3-diazacyclopentane ring moieties in the macrotricyclic ligand are situated oppositely with respect to the square coordination plane in both complexes. This *anti* conformation in $[Cu(L)(ClO_4)_2]$ is similar to that in $[Ni(L)]Cl_2\cdot H_2O$, but different from the *syn* conformation in $[Cu(L)Cl]ClO_4$ where the two ring moieties are situated in the same direction. When the corresponding atoms in the ligands A and B are superimposed using the least-squares fitting methods, the *r.m.s.* deviation is 0.073 Å. The *r.m.s.* deviations between the ligand of $[Ni(L)]Cl_2\cdot H_2O$ and those of A and B are 0.129 and 0.099 Å, respectively.

There are two coordinated tertiary nitrogens N(6) and N(6′), two coordinated secondary nitrogens N(3) and N(3′), and two uncoordinated tertiary nitrogens N(1) and N(1′), in the ligands. The Cu-N(*sec*), Cu-N(*tert*) and Cu-O coordination distances are 1.958 (14), 2.055 (14) and 2.757 (13) Å for the complex A and 1.996 (10), 2.040 (11) and 2.660 (13) Å for the complex B, respectively. The Cu-N distances are in good agreement with those of other Cu(II) complexes[9,13]. Average Cu-N bond distance involving tertiary N(6) is longer by 4σ than that involving secondary N(3), which was also observed for $[Ni(L)]Cl_2\cdot H_2O$. N-methylation of the secondary nitrogen donors in the Ni(II) macrocyclic complexes results in the decrease of the ligand field strength and the lengthe-

*Table of the anisotropic thermal parameters, the coordinates of the hydrogen atoms and the observed and calculated structure factors (12 pp.) are available as the supplementary materials from the author.

**Table 1.** Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2$) for Nonhydrogen Atoms with *e.s.d.*'s in Parentheses

| atom* | A | | | | B | | | |
|---|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | $U_{eq}$** | *x* | *y* | *z* | $U_{eq}$** |
| Cu | 5000 | 0 | 0 | 0.031 | 0 | 5000 | 5000 | 0.031 |
| N(1) | 1887 (22) | 3431 (18) | 102 (11) | 0.060 | 573 (18) | 4562 (18) | 2845 (9) | 0.048 |
| C(2) | 1558 (28) | 2154 (35) | 919 (17) | 0.092 | 2145 (23) | 3658 (22) | 3159 (11) | 0.051 |
| N(3) | 2518 (19) | 560 (18) | 607 (11) | 0.057 | 1709 (14) | 3225 (13) | 4198 (8) | 0.031 |
| C(4) | 2287 (26) | −625 (24) | 1413 (14) | 0.067 | 3228 (19) | 2582 (20) | 4582 (12) | 0.042 |
| C(5) | 3536 (28) | −2450 (33) | 1095 (14) | 0.086 | 2665 (24) | 2335 (21) | 5577 (14) | 0.060 |
| N(6) | 5314 (19) | −2348 (18) | 680 (10) | 0.054 | 1402 (15) | 3908 (14) | 5951 (8) | 0.031 |
| C(7) | 6380 (30) | −2750 (28) | 1352 (17) | 0.082 | 2231 (21) | 5057 (21) | 6164 (12) | 0.047 |
| C(8) | 8138 (26) | −3240 (22) | 777 (14) | 0.060 | 850 (23) | 6171 (21) | 6869 (13) | 0.053 |
| C(9) | 6412 (25) | −3649 (23) | 0 (17) | 0.077 | 195 (22) | 3717 (20) | 6877 (11) | 0.045 |
| Cl | 6900 (6) | 1399 (6) | 1673 (3) | 0.053 | −2468 (5) | 1652 (5) | 5936 (3) | 0.052 |
| O(1) | 8212 (21) | 1027 (28) | 872 (13) | 0.127 | −1757 (30) | 54 (21) | 6354 (14) | 0.102 |
| O(2) | 5459 (17) | 1138 (18) | 1457 (10) | 0.076 | −1145 (25) | 2369 (27) | 5526 (12) | 0.094 |
| O(3) | 6476 (27) | 3057 (19) | 1897 (17) | 0.138 | −3616 (30) | 2771 (34) | 6557 (18) | 0.139 |
| O(4) | 7474 (29) | 292 (26) | 2355 (14) | 0.138 | −3111 (21) | 1429 (20) | 5221 (11) | 0.096 |
| O(2′) | | | | | −270 (13) | 345 (11) | 592 (7) | 0.055 (23) |
| O(3′) | | | | | −395 (12) | 138 (13) | 669 (7) | 0.051 (25) |
| O(4′) | | | | | −96 (11) | 70 (11) | 635 (6) | 0.045 (22) |

*The site occupancy factors for Cu(A) and Cu(B) are 0.5, those for O(2B), O(3B) and O(4B) 0.861 and those for O(2′), O(3′), O(4′) 0.139. The positional parameters $\times 10^3$ for primed O's. $U_{iso}$ for primed O's. **$U_{eq} = 1/3(\Sigma_i \Sigma_j U_{ij} \mathbf{a}_i^* \mathbf{a}_j^* \mathbf{a}_i \mathbf{a}_j)$.

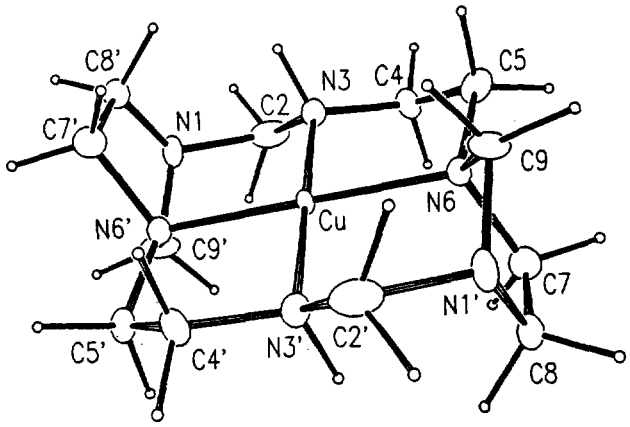



**Figure 1.** ORTEP view of the complex with the atomic numbering scheme.

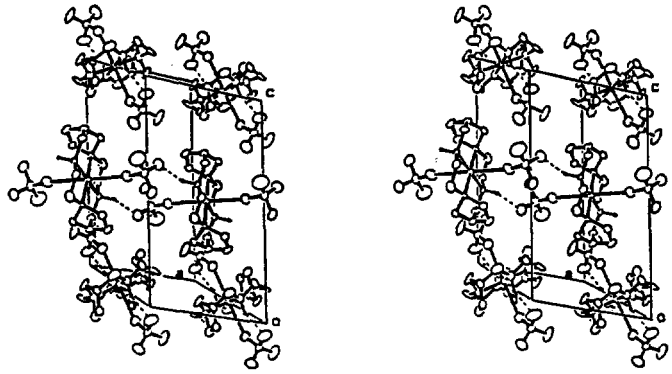


**Figure 2.** A stereoscopic packing diagram. Two complexes in the middle of the figure are B and the other four complexes are A. The O atoms of the perchlorate B in the minor sites and the H atoms except those for the hydrogen bonds are omitted for clarity. The dashed lines denote the hydrogen bonds.

ning of the Ni-N bond[14]. The N4 basal coordination plane is a perfect plane due to symmetry. The Cu-O bonds are relatively weak. The Cu-O distance in the other Cu macrocyclic complexes with the coordinated perchlorate ions varies from 2.463 to 2.744 Å.[15-18] The angles between the Cu-O(2) bonds and the basal nitrogen donors are as follows. The N(3)-Cu-N(6) and N(3)-Cu-N(6′) bite angles are 87.7 (6) and 92.3 (6)° in A and 85.6 (5) and 94.4 (5)° in B, respectively. The O(2)-Cu-N(3) and O(2)-Cu-N(6) angles are 88.7 (5) and 89.9 (5)° in A and 76.2 (5) and 83.1 (5)° in B, respectively. The distances between Cu and uncoordinated tertiary N(1) are 3.193 (14) and 3.238 (13) Å for A and B, respectively. The maximum separation in the macrocyclic rings occur between Cu and ligand atom C(8) with distances of 3.438 (17) Å and 3.494 (17) Å for A and B, respectively. The distances between Cu and Cl are 3.902 (4) Å and 3.962 (4) Å for A and B, respectively. Both 14-membered macrocyclic rings are ruffled and each contains two five- and two six-membered chelate rings. The five-membered chelate rings assume a half-chair conformation. The N-C-C-N torsion angles in the ethylene moieties are 53.0 (16)° in A and 54.3 (13)° in B. The bite distances are 2.800 (19) Å in A and 2.743

**Table 2.** Selected Bond Distances (Å) and Bond Angles (°) with *e.s.d.*'s in Parentheses

| | A | B | | A | B |
|---|---|---|---|---|---|
| Cu-N(3) | 1.985 (14) | 1.996 (10) | Cu-N(6) | 2.055 (14) | 2.040 (11) |
| Cu-O(2) | 2.757 (13) | 2.660 (19) | C(2)-N(3) | 1.401 (30) | 1.529 (19) |
| N(3)-C(4) | 1.465 (24) | 1.472 (18) | C(4)-C(5) | 1.611 (31) | 1.455 (27) |
| C(5)-N(6) | 1.502 (24) | 1.479 (19) | N(6)-C(7) | 1.481 (26) | 1.509 (19) |
| N(6)-C(9) | 1.513 (24) | 1.515 (19) | C(7)-C(8) | 1.467 (28) | 1.514 (23) |
| C(8)-N(1') | 1.380 (25) | 1.483 (21) | N(1')-C(9) | 1.494 (25) | 1.461 (21) |
| C(2')-N(1') | 1.538 (28) | 1.470 (21) | | | |
| Cl-O(1) | 1.399 (18) | 1.415 (15) | Cl-O(2) | 1.445 (13) | 1.413 (18) |
| Cl-O(3) | 1.404 (16) | 1.375 (25) | Cl-O(4) | 1.359 (19) | 1.407 (17) |
| N(6)-Cu-N(3) | 87.7 (6) | 85.6 (5) | N(6)-Cu-N(3') | 92.3 (6) | 94.4 (5) |
| O(2)-Cu-N(3) | 88.7 (5) | 76.2 (5) | O(2)-Cu-N(6) | 89.8 (5) | 83.1 (5) |
| O(2)-Cu-N(3') | 91.3 (5) | 103.8 (5) | O(2)-Cu-N(6') | 90.1 (5) | 96.9 (5) |
| C(2)-N(3)-Cu | 121.4 (13) | 118.3 (9) | C(4)-N(3)-Cu | 108.7 (11) | 106.3 (9) |
| C(5)-N(6)-Cu | 105.7 (12) | 106.1 (10) | C(7)-N(6)-Cu | 114.7 (12) | 112.5 (9) |
| C(9)-N(6)-Cu | 108.6 (11) | 109.0 (9) | C(4)-N(3)-C(2) | 105.3 (16) | 113.1 (12) |
| C(5)-C(4)-N(3) | 106.1 (15) | 108.7 (13) | N(6)-C(5)-C(4) | 108.7 (17) | 109.9 (14) |
| C(7)-N(6)-C(5) | 113.7 (15) | 112.7 (12) | C(8)-C(7)-N(6) | 103.5 (18) | 105.1 (12) |
| C(8)-N(1')-C(2') | 122.7 (16) | 118.1 (13) | N(1)-C(2)-N(3) | 106.3 (18) | 110.4 (12) |
| N(1')-C(8)-C(7) | 109.5 (17) | 106.0 (13) | N(1')-C(9)-N(6) | 99.2 (14) | 103.0 (12) |
| C(9)-N(6)-C(5) | 114.0 (15) | 116.1 (12) | C(9)-N(6)-C(7) | 100.3 (15) | 100.5 (11) |
| C(9)-N(1')-C(8) | 104.7 (16) | 105.1 (12) | C(9)-N(1')-C(2') | 109.8 (15) | 112.5 (13) |
| Cl-O(2)-Cu | 134.0 (8) | 151.8 (13) | | | |

(16) Å in B. The six-membered chelate rings assume a conformation intermediate beween the normal and half-chair conformations. The intracyclic torsion angles range from 38.1 (16) to 87.4 (17)° in A and from 32.5 (10) to 89.9 (14)° in B. The bite distances are 2.914 (19) Å in A and 2.962 (14) Å in B. The 1,3-diazacyclopentane ring moieties assume an envelope conformation with the N-C-C-N torsion angles of −10.8 (15)° in A and −10.0 (12)° in B. Two centrosymmetrically related ring moieties are almost perpendicular to the basal coordination planes with the dihedral of 81.7° in A and 82.7° in B.

The N(3) and N(3') atoms are hydrogen-bonded to the perchlorate O atoms but the complexes A and B have different hydrogen-bonding patterns. Complex A forms intramolecular hydrogen bonds between N(3A) and O(1A) of the coordinated perchlorate ions [N(3A)···O(1A) (1−*x*, −*y*, −*z*), 3.107 (23) Å; H···O(1A), 2.14 (2) Å: N(3A)−H···O(1A) 147.6 (14)°]. Complex B forms intermolecular hydrogen bonds between N(3B) and O(1B) of the perchlorate ions coordinated to the Cu ions which are translated along the *b*-axis [N (3B)···O(1B) (−*x*, −*y*, 1−*z*), 3.025 (19) Å: H···O(1B), 2.13 (2) Å: N(3B)−H···O(1B) 138.1(12)°].

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# The Hydrogen Atom in Interstices of Pd Cluster

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The electronic structure change caused by insertion of hydrogen into the interstices of Pd cluster is studied. Several properties such as energy, reduced overlap population (ROP), electon density (ED) and density of states (DOS) are calculated by Extended Hückel Method. Various types of clusters are considered. The same is performed on Ni and Pt and all the results are compared. The results show that the hydrogen atom in Pd is stabilized remarkably but its wave function is almost unperturbed. The fact is compatible with noticeable solubility of hydrogen in Pd but may not be a positive enough evidence to rationalize the claimed cold fusion phenomenon. It is also found that a remarkable charge transfer from Pd atom to hydrogen atom occurs.

## Introduction

Pons and Fleishmann reported an unusual phenomenon[1] that the fusion reaction can occur at room temperature by the electrochemical method. Its reproducibility[2] and other related study such as physical and chemical investigations[3-16] of Palladium-Hydrogen (Pd-H) systems have reported. Quantum mechanical and theoretical calculations for simple Pd cluster were also performed[17-25]. In fact, the concern for metal-hydrogen system[26-28] began about a century ago[29] and high solubility of hydrogen in Pd has caused keen interests in Pd-H system[30-78].

The aim of this study is to assess the electronic structure change caused by insertion of hydrogen into Pd. The question is of statics that 'How hydrogen exists in Pd' rather than of dynamics that 'How hydrogen enters Pd'. Scanning tunneling microscope (STM)[79-81] has presented photographs for metals[82-88], including Pd, which reveal the extreme roughness of these surfaces. As most electrochemical reactions occur in these rough surfaces, it is reasonable to regard this phenomenon as a reaction between small Pd cluster and hydrogen. Therefore, here, it seems that the molecular orbital (MO) calculation is more appropriate than band calculation[89]. Christensen[23] and Lohr[24] have reported that the hydrogen would exist as atomic entity in Pd. So we assume that the hyrogen exists as atomic form in the interstice of the Pd cluster. This article is divided into three parts as follows.

**Part I.** The electronic structure of atomic hydrogen perturbed by crystal field potential[90,91] is studied by variational method. Six Pd atoms are arrayed to form an octahedron and each atom is regarded as a point charge. A hydrogen atom is put into the center of the octahedron, and then its energy and eigenstate are computed. The same is performed on the hydrogen atom in a tetrahedral field.

**Part II.** A face centered cubic cluster of 44 Pd atoms, with 19 octahedral and 32 tetrahedral interstices, is constructed. After inserting hydrogen atoms into the interstices of the cluster, the energy and electronic structure of the system are studied by Extended Hückel method[92-94].

**Part III.** The clusters of Ni and Pt are compared with that of Pd. The f.c.c. clusters of 32 metal and 32 hydrogen atoms are constructed, respectively, and then they are interwoven to form an NaCl-like structure. The systems are studied as in part II and the difference of the results for three metal are analysed.

Definitions of quantities used throughout the text are given in appendix.

## Calculation and Results

### Part I. Perturbation on Hydrogen Atom Located in Octahedral and Tetrahedral Potential.

A hydrogen atom is at the center of 6 or 4 charge field as shown in Figure 1. The field is of the cubic symmetry. This is one of the simple model potential which a hydrogen atom would experience when it is located at the center of octahedral or tetrahedral interstices of Pd. In fact, if the distance of Pd-H is large enough, the interaction between two atoms would be of purely electrostatic nature.

Total Hamiltonian of the system under the octahedral field can be written as

$$H = H_0 + V_{O_h} \tag{1}$$

where $H_0$ is the total Hamiltonian of isolated hydrogen atom and $V_{O_h}$ is perturbation from 6 point charges. Using atomic unit, each term can be expressed as

$$H_0 = -\nabla^2/2 - 1/r \tag{2}$$