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Crystal Structure of Dichlorobis(cyclohexanone oxime)palladium*1

Masamitsu TANIMURA,*2 Toshio MIZUSHIMA and Yukio KINOSHITA

Basic Research Laboratories, Toyo Rayon Company, Kamakura

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The crystal structure of dichlorobis(cyclohexanone oxime)palladium, $PdCl_2(C_6H_{10}NOH)_2$, has been determined from three-dimensional X-ray photographic data. The crystals belong to the triclinic space group $P\bar{1}$, with these cell parameters: $a=8.81$ Å, $b=9.19$ Å, $c=4.99$ Å; $\alpha=91°32'$, $\beta=99°41'$ and $\gamma=102°02'$. The unit cell contains one molecule of the complex. The palladium atoms are spaced at intervals of 4.99 Å along the c-axis and have a square planar coordination, with two chlorine atoms at 2.24 Å and two nitrogen atoms of the oxime group at 2.08 Å. The complexes are hydrogen-bonded with each other in strings of indefinite length along the c-axis, and the hydrogen bond distance between the oxygen atom of the hydroxyimino group and the chlorine atom is 2.93 Å.

Dichlorobis(cyclohexanone oxime)palladium, $PdCl_2(C_6H_{10}NOH)_2$, is a novel and stable metal complex between an oxime and palladium chloride, but no conclusive findings about its structure have been obtained. This compound was isolated while we were investigating the reduction of α-chloro oximes with various catalysts, among which palladium chloride was found to be most effective, affording oximes in excellent yields.[1] The present investigation was carried out in order to determine the detailed structure of the complex by X-ray diffraction techniques.

Experimental

Crystals of dichlorobis(cyclohexanone oxime) palladium complex were prepared by mixing palladium chloride and cyclohexanone oxime in a cyclohexane-tetrahydrofuran mixture, and were recrystallized from an ethyl alcohol solution. The crystals are yellow needles with their principal faces (010), elongated in the c direction.

The cell-dimension data were obtained from rotation and zero-level Weissenberg films, taken about the three axes. The cell parameters are:

$a = 8.81 \text{ Å} \pm 0.01 \text{ Å}$ $\quad \alpha = 91°32' \pm 6'$

$b = 9.19 \text{ Å} \pm 0.01 \text{ Å}$ $\quad \beta = 99°41' \pm 6'$

$c = 4.99 \text{ Å} \pm 0.01 \text{ Å}$ $\quad \gamma = 102°02' \pm 6'$

There were no systematic extinctions, indicating, along with the Laue symmetry, that the space group is either $P1$ or $P\bar{1}$. The density, as measured by flotation in an ethyl iodide-toluene mixture at 25°C, is $D_m=1.71$ g·cm^{-3}, while that calculated for $Z=1$ is $D_x=1.72$ g·cm^{-3}. Therefore, the unit cell contains one formula unit of $PdCl_2(C_6H_{10}NOH)_2$.

The intensities were recorded on equi-inclination Weissenberg photographs with both multi-film and varying exposures, using Cu$K\alpha$ radiation. Zero to fifth layers about [a], with a cross section of 0.06×0.09 mm, and zero to fourth layers about [c], with a cross section of 0.06×0.05 mm, were recorded. No absorption corrections were made. The intensities were estimated visually, correlated by means of common reflections, and reduced to the 1530 observed relative structure amplitudes, using Van den Hende's IBM 7090 data reduction program.[2]

Structure Determination

The space group was assumed to be $P\bar{1}$, this choice of space group was corroborated by the structure determination. The palladium atom was assigned to the (0, 0, 0) position.

The Patterson projection, $P(x, y)$, was calculated from the values of F^2 for the ($hk0$) reflections, and approximate x- and y-coordinates of all the atoms except hydrogen were obtained. A Fourier synthesis of the electron density projected along the c-axis was computed; an ($hk0$) structure factor calculation based on this model gave an agreement index of $R=0.24$. The parameters were refined on an IBM 7090 computer with the least-squares program of Van den Hende[3]; five cycles of the calculations reduced R to 0.17.

The Patterson projection, $P(y, z)$, was then calculated for the ($0kl$) reflections, and approximate z-coordinates were obtained by referring to y-coordinates obtained from $P(x, y)$. The agreement index for the ($0kl$) was 0.16. Since there was little resolution of the atoms on this projection, the complete three-dimensional data were further refined.

*1 Presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1964.

*2 Present address: Central Research Laboratories, Toyo Rayon Company, Otsu.

1) Toyo Rayon Co., Ltd., Japanese Pat. 41-5445 (1966).

2) J. H. Van den Hende, "A Fortran Program for the Correction of X-ray Intensity Data" (1962).

3) J. H. Van den Hende, "Crystallographic Structure Factor and Least-Squares Refinement Program for the IBM 7090" (1961).

A Fourier synthesis of the three-dimensional electron density distribution was also carried out, and the positions of all the atoms except hydrogen atoms were determined. Five cycles of refinement were computed using Van den Hende's IBM 7090 least-squares program. The R factor thus dropped from 0.186 to 0.142. The final atomic coordinates and isotropic temperature factors are listed in Table 1, while the observed and calculated structure factors are listed in the table kept at the office of this Bulletin.*3

TABLE 1. ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

	x	y	z	B(Å^2)
Pd	0	0	0	3.14
Cl	0.1963	0.1168	0.3301	4.75
O	0.0473	0.2828	0.6714	5.65
N	0.9523	0.1961	0.8449	4.12
C_1	0.8473	0.2608	0.9070	4.35
C_2	0.8269	0.4157	0.7901	5.07
C_3	0.6495	0.4132	0.6822	5.48
C_4	0.5496	0.3436	0.8926	5.39
C_5	0.5667	0.1817	0.9784	6.07
C_6	0.7412	0.1791	0.0992	5.11

Results and Discussion

The atomic arrangement in the crystal is shown in Fig. 1 and Fig. 2. The interatomic distances and bond angles are given in Table 2.

*3 The complete data of the F_o-F_c table are kept as Document No. 6707 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and by remitting, in advance, ¥ 300 for photoprints. Pay by check or money order poyable to: Chemical Society of Japan.

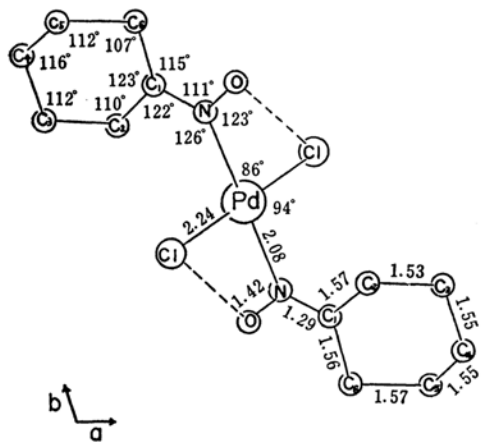

Fig. 1. The molecule viewed down c. No hydrogen atoms are shown. The origin is at the palladium atom.

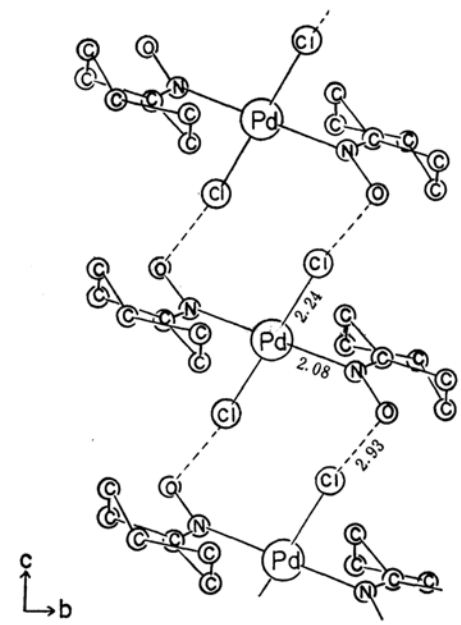

Fig. 2. The molecule viewed down a. No hydrogen atoms are shown. The origin is at the palladium atom.

The palladium atoms at the center of symmetry are spaced at intervals of 4.99 Å along the c-axis, and have a square planar coordination, with two chlorine atoms at 2.24 Å and two nitrogen atoms of the oxime group at 2.08 Å; Pd-N makes an angle of 94° with Pd-Cl. As is shown in Fig. 2, the complexes are hydrogen-bonded with each other in strings of indefinite length along the c-axis, and the hydrogen bond distance between the oxygen atom of the hydroxyimino group and the chlorine atom is 2.93 Å. The cyclohexane ring takes a chair form, and the C–C bond lengths are normal.

TABLE 2. INTERATOMIC DISTANCES AND BOND ANGLES

Pd-Cl	2.24 Å	Cl-Pd-N	86°
Pd-N	2.08	Cl′-Pd-N	94
O-N	1.42	Pd-N-O	123
N-C_1	1.29	Pd-N-C_1	126
C_1-C_2	1.57	O-N-C_1	111
C_2-C_3	1.53	N-C_1-C_2	122
C_3-C_4	1.55	C_6-C_1-C_2	123
C_4-C_5	1.55	C_1-C_2-C_3	110
C_5-C_6	1.57	C_2-C_3-C_4	112
C_6-C_1	1.56	C_3-C_4-C_5	116
		C_4-C_5-C_6	112
		C_5-C_6-C_1	107

The atoms C_1, C_2, C_6, N, and O are almost coplanar, and the least-squares plane through these atoms is given by the equation;

$$0.4791X + 0.3734Y + 0.7697Z = 7.9580$$

Table 3. Departures from the least-squares plane

O	0.01 Å
N	−0.02
C_1	−0.00
C_2	−0.00
C_6	0.01

As Table 3 shows, deviations of the atoms from this plane appear not to be significant.

The distance of the C_1–N bond (1.29 Å) suggests its double-bond character and may be compared to the value, 1.29 Å, found in acetoxime.[4]

The coplanarity of the atoms, C_1, C_2, C_6, N, and O is due to the double bond character of the C–N bond.

The angle C_3–C_4–C_5 is distorted to 116° from a normal tetrahedral value (109.5°); this distortion would be affected by the angle C_6–C_1–C_2 (123°).

4) T. K. Bierlein and E. C. Lingafelter, *Acta Cryst.*, **4**, 450 (1951).

As is usually accepted, all the intermolecular approaches observed are equall to or longer than the sum of the van der Waals radii of the corresponding atoms, within the limit of experimental error.

The crystals showed a mp of 184°C (dec.) and a magnetic susceptibility of $\chi_M = -220 \times 10^{-6}$ c. g. s. e. m. u. when measured by Professor M. Kubo and Dr. M. Kishita of Nagoya University and Dr. Y. Kurita of our laboratories. The infrared spectrum of the complex in the solid state (KBr pellet) exhibited only a strong absorption at 3190 cm^{-1}, showing the presence of a hydrogen bonding of the hydroxyl group, and a medium absorption at 1660 cm^{-1} (hydroxyimino group).

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