The Crystal Structure of Dichlorobis(acetoxime)palladium

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The crystal structure of dichlorobis(acetoxime)palladium, $PdCl_2(C_3H_6NOH)_2$, has been determined from three-dimensional single-crystal X-ray photographic data. The crystals belong to the monoclinic system (space group $P2_1/a$), with two formula units in a cell with dimensions: $a=8.709\pm0.007$, $b=13.996\pm0.005$, $c=4.756\pm0.006$ Å, and $\beta=95.60\pm0.05°$. The structure was established by the heavy-atom method and was refined by the block-diagonal least-squares procedure. The Pd atoms are spaced at intervals of 4.76 Å along the c-axis and have a *trans* planar coordination, with two Cl atoms at 2.30 Å and two N atoms of the oxime groups at 2.03 Å. The oxime plane is twisted about the Pd–N bond by 72.7° from the coordination plane defined by the Pd, Cl, and N atoms. The complex molecules are hydrogen-bonded with each other in strings of an indefinite length along the c-axis, and the hydrogen-bond distance between the O atom of the oxime and the Cl atom is 3.07 Å.

As part of a systematic study of the crystal structures of the palladium-complexes, the crystal structures of the stable monoxime-palladium complexes have been investigated in order to ascertain the conformational features around the metals. In the previous papers of this series, the crystal structures of $PdCl_2(C_6H_{10}NOH)_2$[1] and $[Pd(\pi\text{-}C_3H_5)Cl]_2C_6H_{10}NOH$[2] were descrived. In this investigation the crystal of dichlorobis(acetoxime)-palladium was subjected to X-ray crystal-structure analysis in order to obtain structural information.

Experimental

Dichlorobis(acetoxime)palladium, $PdCl_2(C_3H_6NOH)_2$, was prepared by mixing palladium chloride and acetoxime[3] and was recrystallized from a tetrahydrofuran solution as a reddish yellow crystal elongated in the c direction. The unit-cell dimensions were determined from Weissenberg and precession photographs, taken about the three axes. The density was measured by flotation in an ethyl iodide-toluene mixture at 25 °C. The crystal data are summarized in Table 1.

The three-dimensional intensity data were collected from equi-inclination Weissenberg photographs taken with Ni-filtered CuKα radiation. The multiple-film technique was used, and the layers from zero to first about the a-axis and those from zero to third about the c-axis were recorded. The relative intensities, estimated visually by comparison with a calibrated intensity scale, were corrected for the usual Lorentz and polarization factors. No corrections were made for the small absorption errors. A total of 841 independent reflections was used for the structure determination.

TABLE 1. CRYSTAL DATA

Dichlorobis(acetoxime)palladium, $C_6H_{14}N_2O_2Cl_2Pd$
Molecular weight: 323.5
Monoclinic
$a=8.709\pm0.007$Å
$b=13.996\pm0.005$
$c=4.756\pm0.006$
$\beta=95.60\pm0.05°$
$V=576.8$ Å^3
$D_m=1.83$ g·cm^{-3}, $D_x=1.862$ g·cm^{-3} for $Z=2$
Systematic absences, $h0l$ with $h=2n+1$
$0k0$ with $k=2n+1$
Space group $C_{2h}^5-P2_1/a$ (No. 14)

Structure Determination

The structure was established by the heavy-atom method. Since there are two molecules in the cell of the $P2_1/a$ space group, the palladium atoms must be at the centers of symmetry. The position of the chlorine atom was readily deduced from a three-dimensional sharpened Patterson synthesis. The successive Fourier syntheses phased initially by the palladium and chlorine atoms enabled the positions of the carbon, nitrogen, and oxygen atoms of the oxime to be determined and resulted in a reduction of R to 0.258. R is defined throughout as $\Sigma||F_o|-|F_c||/\Sigma|F_o|$, where the sums are over the unique, observed non-zero reflections only. The structure thus obtained was refined by the least-squares method. Four cycles of least-squares refinement using individual isotropic temperature factors, followed by one cycle using individual anisotropic temperature factors, reduced R to 0.132. Three more cycles of refinement of the non-hydrogen atoms with anisotropic temperature factors led to a final R-index of 0.083. Throughout the refinement of the structure, equal weights were employed for all the reflections and the atomic scattering factors were adopted from the International Tables for X-ray Crystallography.[4] The main part of the calculations was performed

TABLE 2. THE ATOMIC COORDINATES OF DICHLOROBIS-(ACETOXIME)PALLADIUM, ALONG WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x/a	y/b	z/c
Pd	0	0	0
Cl	0.0960(4)	0.1176(4)	−0.2705(5)
O	0.2997(11)	0.0165(12)	0.3287(13)
N	0.2201(11)	−0.0410(11)	0.1174(13)
C(1)	0.2278(17)	−0.1722(18)	−0.1906(20)
C(2)	0.2982(14)	−0.1099(16)	0.0257(16)
C(3)	0.4663(15)	−0.1263(18)	0.1463(19)

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TABLE 3. ANISOTROPIC THERMAL PARAMETERS IN THE FORM OF
$\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$
Each value is multiplied by 10^4 and the estimated standard deviations are shown in parentheses.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	69(2)	43(0)	420(9)	6(2)	15(6)	−23(5)
Cl	106(5)	48(2)	542(26)	−6(6)	54(17)	−2(12)
O	125(17)	60(7)	732(85)	−2(18)	12(59)	−84(39)
N	87(16)	44(6)	421(76)	−2(17)	−32(55)	19(35)
C(1)	140(27)	62(11)	660(86)	76(28)	−109(89)	−90(59)
C(2)	94(20)	60(10)	396(94)	18(23)	141(67)	66(47)
C(3)	86(22)	71(11)	688(86)	26(25)	12(80)	25(60)

on IBM 7090 and 360 computers using the ERFR 2 program for Fourier synthesis[5] and the HBLS IV program for the structure-factor and least-squares-refinement calculations.[6] The positional and anisotropic thermal parameters, along with their estimated standard deviations, are listed in Tables 2 and 3 respectively. The tables of the final observed and calculated structure factors are preserved by the Chemical Society of Japan (Document No. 7424).

Results and Discussion

The principal interatomic bond lengths and angles, along with their estimated standard deviations, are listed in Table 4. A perspective view of the molecule,

TABLE 4. INTERATOMIC DISTANCES AND ANGLES ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atoms	Distance	Atoms	Angle
Pd-Cl	2.30(2) Å	Cl-Pd-N	88.3(0.5)°
Pd-N	2.03(2)	Pd-N-O	114.8(0.5)
N-O	1.41(3)	Pd-N-C(2)	129.8(0.5)
N-C(2)	1.28(3)	O-N-C(2)	115.5(0.5)
C(1)-C(2)	1.44(3)	N-C(2)-C(1)	119.8(0.5)
C(2)-C(3)	1.53(3)	N-C(2)-C(3)	120.3(0.5)
		C(1)-C(2)-C(3)	120.1(0.5)

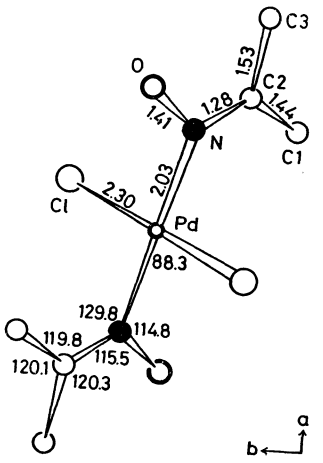

Fig. 1. A perspective view of the molecule along the c-axis.

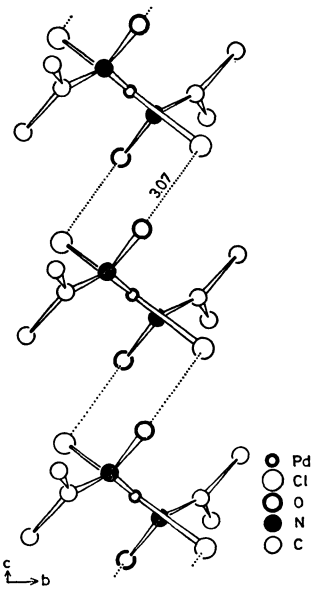

Fig. 2. The molecular arrangement viewed down the a-axis. The hydrogen bonds are shown by dotted lines.

with the numbering of atoms, as viewed along the c-axis is shown in Fig. 1. Figure 2 represents the mode of hydrogen bonding and the molecular arrangement viewed down the a-axis.

The crystal structure of dichlorobis(acetoxime)palladium closely resembles that of dichlorobis(cyclohexanone oxime) palladium.[1] The palladium atoms at the centers of symmetry are spaced at intervals of 4.75 Å along the c-axis and are coordinated in a square-planar configuration by two chlorine atoms and two nitrogen atoms of the oximes, the Pd–Cl and Pd–N distances being 2.30 and 2.03 Å respectively. As Fig. 2 shows, the complexes are hydrogen-bonded with each other in strings of an indefinite length along the *c*-axis; the distance between the oxygen atoms of the oxime groups and the chlorine atoms is 3.07 Å. The bond distances and angles in this complex are compared with the corresponding ones in $PdCl_2$-$(C_6H_{10}NOH)_2$[1] and $[Pd(\pi\text{-}C_3H_5)Cl]_2C_6H_{10}NOH$[2] in Table 5. The Pd–Cl bond length of 2.30 Å is longer than the value of 2.24 Å in $PdCl_2(C_6H_{10}NOH)_2$, but is in good agreement with those found in $(PdCl_2)_n$ (2.31 Å),[7] $C_7H_8PdCl_2$ (2.31 Å),[8] and $[(C_6H_5CN)$-$PdCl_2]_2$ (2.35 Å).[9] The Pd–N bond length of 2.03 Å

TABLE 5. COMPARISON OF THE SELECTED INTERATOMIC BOND DISTANCES AND ANGLE IN SOME PALLADIUM-OXIME COMPLEXES

Atom	$PdCl_2(C_3H_6NOH)_2$[a]	$PdCl_2(C_6H_{10}NOH)_2$[1]	$[Pd(\pi\text{-}C_3H_5)Cl]_2\cdot C_6H_{10}NOH$[2]
Pd-Cl	2.30 Å	2.24 Å	2.41—2.45 Å
Pd-N	2.03	2.08	2.10
N-O	1.41	1.42	1.39
N-C	1.28	1.29	1.28
Cl-O	3.07[b]	2.93[b]	3.03[c]
Cl-Pd-N	88.3°	86°	92.1°

a) Present work. b) Intermolecular hydrogen bond. c) Intramolecular hydrogen bond.

is a little shorter than the lengths in $PdCl_2(C_6H_{10}NOH)_2$ and $[Pd(\pi\text{-}C_3H_5)Cl]_2C_6H_{10}NOH$. It, however, agrees well with the values of 2.031 Å in bis-(*N*-isopropyl-3-ethylsalicylaldiminato) palladium,[10] 2.032 Å in the tetragonal form of bis-(*N*-isopropyl-3-methylsalicylaldiminato)palladium,[11] and 2.032 and 2.043 Å in bis(ethylenediamine)palladium(II) chloride.[12]

The C–C bond lengths in the oxime group of 1.44 and 1.53 Å found here are not greatly different from the corresponding values for the other oximes[13] which lie between 1.44 and 1.56 Å. The C–N bond distance of 1.28 Å suggests its double-bond character and is comparable to similar distances in acetoxime and other oximes.[14] Although the present value of 1.41 Å for the N–O bond length appears to be somewhat shorter than the values obtained for acetoxime, it is probably not unwarranted when it is compared with the values of 1.41 Å in formamidoxime,[15] 1.42 Å in $PdCl_2(C_6H_{10}NOH)_2$, and 1.39 Å in $[Pd(\pi\text{-}C_3H_5)Cl]_2C_6H_{10}NOH$.

The palladium coordination plane, as defined by the Pd, Cl, and N atoms, is expressed by the equation:[16]

$$0.048\,X + 0.805\,Y + 0.998\,Z = 0$$

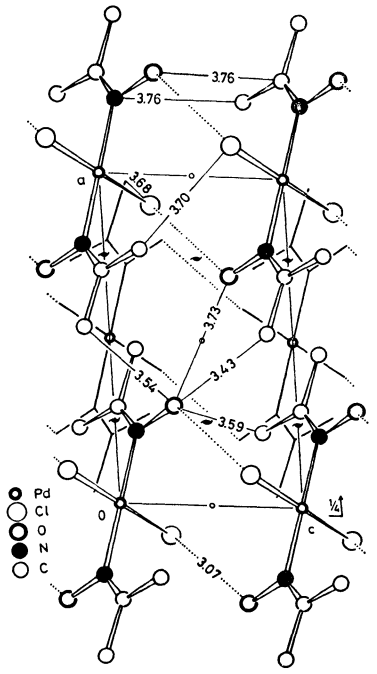

Fig. 3. The crystal structure projected along the b-axis. The intermolecular atomic contacts less than 3.8 Å are shown by solid lines and the hydrogen bonds are shown by dotted lines.

The equation for the best-plane containing O, N, C(1), C(2), and C(3) atoms is:

$$-0.389\,X - 0.748\,Y + 0.920\,Z = 0.024.$$

The deviations of the five atoms from this plane are within 0.01 Å. The chlorine atom at the $(x, y, c+z)$ position, which is connected by a hydrogen bond with the oxygen atom of the oxime, is separated from this plane by 1.54 Å. The dihedral angle between the oxime plane and the palladium coordination plane is 72.7°, which is comparable to the corresponding value of 81.0° between the palladium square-planar plane and the best-plane of the O–N–C$\langle_{C}^{C}$ fragment of the cyclohexanone oxime in $PdCl_2(C_6H_{10}NOH)_2$.

Figure 3 shows the molecular packing projected along the b-axis. The intermolecular atomic contacts less than 3.8 Å are shown by solid lines. The hydrogen bonds are also shown by dotted lines. None of the atoms is significantly shorter than the normal van der Waals contact.

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16) The equation of the best-plane refers to an orthogonal coordinate system in which *X*, *Y*, and *Z* in Å are parallel to a, b, and c*, respectively.