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CRYSTAL STRUCTURE OF μ-CHLORO-CHLORO-DI-π-ALLYL (CYCLOHEXANONE OXIME) DIPALLADIUM

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SUMMARY

The crystal structure of μ-chloro-chloro-di-π-allyl(cyclohexanone oxime)-dipalladium, $[Pd(\pi\text{-}C_3H_5)Cl]_2C_6H_{10}NOH$, has been determined from three-dimensional X-ray diffraction data collected on a single crystal diffractometer with Mo-$K\alpha$ radiation. The crystals belong to the triclinic space group $P\bar{1}(C_i^1)$, with cell parameters: $a=8.00\pm0.01$ Å, $b=14.47\pm0.01$ Å, $c=7.88\pm0.02$ Å, $\alpha=95.1\pm0.1°$, $\beta=90.3\pm0.2°$, and $- = 113.1\pm0.1°$.

The unit cell contains two molecules of the complex. The complex has a binuclear structure of the two palladium atoms, one coordinates to a π-allyl group and two chlorine atoms in a square-planar configuration. The other palladium atom coordinates to one chlorine atom, a π-allyl group and the nitrogen atom of the oxime, also with a square-planar geometry. The structure may be derived from that of bis-(π-allylpalladium chloride) by rupture of the bond between the palladium and one of the bridge chlorine atoms, coordination of the nitrogen of the oxime to the palladium and formation by the terminal chlorine atom of a hydrogen bond with the hydroxyl group of the oxime. The orientation of the π-allyl groups with respect to the palladium atoms is similar to those found in other π-allyl complexes.

INTRODUCTION

Cyclohexanone oxime forms stable palladium complexes by displacing coordinated ligands of many palladium complexes as reported in the previous paper[1]. Cyclohexanone oxime has a lone pair of electrons on the nitrogen atom, with which it coordinates to the palladium. Tanimura *et al.*[2] have reported the X-ray analysis of the structure of dichlorobis(cyclohexanone oxime)palladium, $PdCl_2(C_6H_{10}NOH)_2$.

In the reaction of cyclohexanone oxime with π-allylpalladium chloride, Tsuji and his co-workers have synthesized a new complex, the analysis of which suggested the molecular formula, $[Pd(C_3H_5)Cl]_2\cdot C_6H_{10}NOH$. Thus one mole of the oxime was apparently incorporated per two palladium atoms in this complex. The NMR and IR spectra showed that the π-allyl system was retained in this complex. From these results the mode of the coordination of oxime in this complex is of special interest. This paper reports three-dimensional X-ray analysis of the complex. It was found that the complex has an unsymmetrical binuclear structure.

EXPERIMENTAL

μ-Chloro-chloro-di-π-allyl(cyclohexanone oxime)dipalladium, $[Pd(\pi\text{-}C_3H_5)Cl]_2C_6H_{10}NOH$, was prepared by the reaction of π-allylpalladium chloride and cyclohexanone oxime in dichloromethane, and recrystallized from a dichloromethane/ether solution at room temperature. The crystals obtained were thin hexangular yellow prisms elongated in the *a* direction. Oscillation and Weissenberg photographs, taken about the three axes using Cu-$K\alpha$ radiation showed that the crystal is triclinic.

The cell parameters are: $a=8.00\pm0.01$ Å, $b=14.47\pm0.01$ Å, $c=7.88\pm0.02$ Å, $\alpha=95.1\pm0.1°$, $\beta=90.3\pm0.2°$, and $\gamma=113.1\pm0.1°$.

There are two formula weights in the unit cell, giving a calculated density of 1.920 $g\cdot cm^{-3}$. The density, measured by flotation in an aqueous mixture of perchloric acid and zinc carbonate at 25°, was 1.926 $g\cdot cm^{-3}$. Of the possible space groups, $P1$ and $P\bar{1}$, the latter was assumed and the successful determination of the crystal structure supported the assumption. A crystal having dimensions of $0.19\times0.20\times0.10$ mm was mounted along the *a* axis and the intensities were measured with zirconium-filtered Mo-$K\alpha$ radiation. The collection of intensity data was made on a Hilger and Watts linear diffractometer[3] equipped with a scintillation counter and a pulse-height discriminator. Each reflection was measured, using a one-minute motor and a 3° oscillation angle. About fifty reflections were set by hand. The intensities of 4195 independent reflections within the range $\sin\theta/\lambda$ $0\sim0.681$ were collected. Of these, 854 reflections had zero intensities and further 281 had intensities more than the standard deviation of the total counts, after the two background readings have been substracted, and were therefore excluded from the analysis.

Throughout data collection three reflections were measured at regular intervals as a check on crystal and instrument stability. Serious crystal decomposition was not found during the collection of intensity data. The usual Lorentz and polarization factors were applied to 3060 intensities to yield relative structure factors. Since the estimated absorption parameter, $\mu\cdot R$, is sufficiently small (0.23), no absorption correction was made.

STRUCTURE DETERMINATION

The coordinates of the two palladium and two chlorine atoms were readily deduced from a three-dimensional Patterson synthesis, and the remaining atoms except hydrogen were found on successive three-dimensional electron density maps phased initially with the palladium and chlorine atoms. Inclusion of these atoms in the structure-factor calculations reduced an R-factor $(=\Sigma||F_o|-|F_c||/\Sigma|F_o|)$ to 0.14 from 0.25. The structure thus obtained was refined by isotropic least-squares method using the program of Van den Hende[4] for an IBM 7040 computer. After a few cycles of this refinement R fell to 0.116. A survey of the Fourier map at this stage showed the effects of anisotropic motions associated with the heavy atoms. After a series of four cycles of positional and anisotropic thermal parameters by the use of the program of Ashida[5], the final R-factor dropped to 0.086 for the 3060 reflections. No difference

Fourier synthesis was computed and the contribution of the hydrogen atoms has not been included in the structure-factor calculations. Equal weights were employed for all reflections. The atomic scattering factors used in all calculations were taken from the International Tables for X-ray Crystallography[6]. The fractional coordinates and

TABLE 1

ATOMIC COORDINATES (WITH STANDARD DEVIATIONS IN PARENTHESES)

Atom	x	y	z
Pd(1)	0.0636(1)	0.1502(1)	0.9592(1)
Pd(2)	0.7229(1)	0.2167(1)	0.2461(1)
Cl(1)	0.7781(4)	0.1687(4)	0.9520(4)
Cl(2)	0.1358(4)	0.2123(4)	0.2621(4)
C(1)	0.0397(24)	0.0789(25)	0.6983(19)
C(2)	0.2109(29)	0.1199(33)	0.7607(24)
C(3)	0.2961(22)	0.1190(24)	0.9070(20)
C(4)	0.5505(21)	0.0666(19)	0.3149(19)
C(5)	0.5161(23)	0.1386(20)	0.4069(20)
C(6)	0.6289(20)	0.2239(23)	0.5008(17)
C(7)	0.8286(19)	0.4401(19)	0.2085(21)
C(8)	0.9661(21)	0.5557(18)	0.2140(23)
C(9)	0.8740(23)	0.6178(21)	0.3080(23)
C(10)	0.6779(20)	0.5928(17)	0.2599(21)
C(11)	0.5560(21)	0.4771(18)	0.2650(28)
C(12)	0.6290(22)	0.4100(24)	0.1559(28)
N	0.8851(11)	0.3714(10)	0.2285(11)
O	0.0745(10)	0.4043(11)	0.2447(10)

TABLE 2

ANISOTROPIC THERMAL PARAMETERS (Å^2) IN THE FORM $\exp[-(B_{11}\cdot h^2+B_{22}\cdot k^2+B_{33}\cdot l^2+B_{12}\cdot h\cdot k+B_{13}\cdot h\cdot l+B_{23}\cdot k\cdot l)]$ (WITH STANDARD DEVIATIONS IN PARENTHESES)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd(1)	0.0174(4)	0.0052(4)	0.0172(4)	0.0079(4)	0.0081(3)	0.0019(4)
Pd(2)	0.0155(4)	0.0047(3)	0.0156(3)	0.0058(4)	0.0052(4)	0.0017(4)
Cl(1)	0.0160(12)	0.0089(4)	0.0154(8)	0.0114(9)	−0.0001(8)	−0.0033(6)
Cl(2)	0.0245(11)	0.0069(4)	0.0184(12)	0.0128(11)	−0.0050(7)	−0.0006(5)
C(1)	0.0415(56)	0.0137(17)	0.0207(36)	0.0228(50)	0.0215(69)	−0.0039(38)
C(2)	0.0542(78)	0.0249(25)	0.0310(45)	0.0487(88)	0.0328(91)	−0.0114(67)
C(3)	0.0328(52)	0.0126(21)	0.0293(41)	0.0261(46)	0.0108(66)	−0.0038(40)
C(4)	0.0335(48)	0.0077(13)	0.0246(39)	0.0065(38)	0.0259(71)	0.0142(39)
C(5)	0.0402(53)	0.0071(11)	0.0262(42)	0.0057(41)	0.0328(78)	0.0065(37)
C(6)	0.0302(44)	0.0117(15)	0.0162(29)	0.0013(43)	0.0149(56)	−0.0015(35)
C(7)	0.0223(38)	0.0068(14)	0.0378(46)	0.0115(32)	0.0015(66)	−0.0005(36)
C(8)	0.0276(46)	0.0048(10)	0.0474(55)	0.0082(27)	0.0130(78)	0.0065(40)
C(9)	0.0357(49)	0.0073(12)	0.0369(57)	0.0101(36)	−0.0006(90)	0.0054(42)
C(10)	0.0279(38)	0.0045(11)	0.0396(51)	0.0095(26)	−0.0031(67)	0.0000(26)
C(11)	0.0253(41)	0.0044(9)	0.0658(70)	0.0068(30)	0.0119(83)	−0.0016(48)
C(12)	0.0239(42)	0.0090(16)	0.0590(65)	0.0103(37)	−0.0173(85)	−0.0009(56)
N	0.0175(18)	0.0037(9)	0.0168(15)	0.0057(18)	0.0055(27)	0.0011(17)
O	0.0173(16)	0.0058(8)	0.0209(17)	0.0050(19)	0.0057(26)	0.0036(16)

anisotropic thermal parameters, with corresponding standard deviations are given in Tables 1 and 2. Final observed and calculated structure factors are available to interested readers.*

RESULTS AND DISCUSSION

The interatomic distances and bond angles are listed in Table 3. Table 4 summarizes the deviations of atoms from some molecular planes. The projection of

TABLE 3

INTERATOMIC DISTANCES, BOND ANGLES, AND DIHEDRAL ANGLES IN $[Pd(\pi\text{-}C_3H_5)Cl]_2C_6H_{10}NOH$

Interatomic distances (Å)			
Pd(1)-Cl(1)	2.405(8)	C(11)-C(12)	1.52(3)
Pd(1)-Cl(2)	2.439(9)	C(12)-C(7)	1.50(3)
Pd(2)-Cl(1)	2.449(7)	C(7)-N	1.28(3)
Pd(2)-Cl(2)	3.331(7)	N-O	1.39(3)
Pd(2)-N	2.10(2)	Pd(1)-C(1)	2.18(2)
C(1)-C(2)	1.32(4)	Pd(1)-C(2)	2.09(2)
C(2)-C(3)	1.34(4)	Pd(1)-C(3)	2.12(2)
C(4)-C(5)	1.33(3)	Pd(2)-C(4)	2.18(2)
C(5)-C(6)	1.33(3)	Pd(2)-C(5)	2.11(2)
C(7)-C(8)	1.59(3)	Pd(2)-C(6)	2.16(2)
C(8)-C(9)	1.52(3)	Pd(1)-Pd(2)	3.910(6)
C(9)-C(10)	1.49(3)	Cl(1)-Cl(2)	3.552(7)
C(10)-C(11)	1.56(4)	Cl(2)-O	3.03(4)[a]
Interatomic angles (°)			
Pd(1)-Cl(1)-Pd(2)	107.3(0.6)	C(12)-C(7)-N	119.9(1.4)
Pd(1)-Cl(2)-Pd(2)	83.8(0.5)	Pd(2)-N-C(7)	126.3(0.9)
Cl(1)-Pd(1)-Cl(2)	94.3(0.5)	Pd(2)-N-O	117.8(0.9)
Cl(1)-Pd(2)-Cl(2)	74.1(0.4)	Pd(2)-Cl(2)-O	56.4(0.7)
C(1)-C(2)-C(3)	126.8(1.8)	Cl(2)-O-N	104.8(1.2)
C(4)-C(5)-C(6)	125.2(1.6)	Cl(1)-Pd(2)-N	92.1(0.7)
C(7)-C(8)-C(9)	106.1(1.2)	Cl(2)-Pd(2)-N	80.7(0.7)
C(8)-C(9)-C(10)	118.5(1.2)	Cl(1)-Pd(1)-C(1)	97.3(0.6)
C(9)-C(10)-C(11)	111.2(1.1)	Cl(2)-Pd(1)-C(3)	98.7(0.8)
C(10)-C(11)-C(12)	111.7(1.2)	C(1)-Pd(1)-C(3)	69.6(1.0)
C(11)-C(12)-C(7)	109.4(1.3)	N-Pd(2)-C(6)	101.4(0.6)
C(12)-C(7)-C(8)	119.1(1.2)	Cl(1)-Pd(2)-C(4)	99.4(0.5)
C(7)-N-O	115.8(1.4)	C(4)-Pd(2)-C(6)	67.9(0.5)
C(8)-C(7)-N	120.5(1.3)	Pd(1)-Cl(2)-O	95.9(0.6)

Dihedral angles (°) *between planes each defined by three atoms*		
(Pd(1), Cl(1), Cl(2)),	(C(1), C(2), C(3))	125(2.9)
(Pd(2), Cl(1), N),	(C(4), C(5), C(6))	119(2.6)

[a] Hydrogen bonding.

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* The Table of structure factors has been deposited as NAPS Document No. 01506, with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 Third Avenue, New York, New York 10022. A copy may be secured by citing the document number and by remitting $2.00 for a microfiche or $5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

TABLE 4

LEAST SQUARES PLANES AND DEVIATIONS (Å) OF ATOMS FROM THE PLANES[a]

Plane (1) defined Pd(1), Cl(1), and Cl(2)

Pd(1)	−0.000	C(1)	0.516
Cl(1)	0.000	C(2)	0.814
Cl(2)	0.000	C(3)	0.114

Eqn.: $0.9531\ X-2.3426\ Y-0.2970\ Z=-5.5502$

Plane (2) defined by Pd(2), Cl(2), and N

Pd(2)	−0.000	C(4)	0.424
Cl(2)	0.000	C(5)	0.450
N	0.000	C(6)	0.167

Eqn.: $0.9496\ X+0.2406\ Y-0.3134\ Z=0.7981$

Plane (3) defined by C(7), C(8), C(12), and N

C(7)	0.045	C(11)	1.061
C(8)	−0.014	C(12)	−0.014
C(9)	0.976	N	−0.017
C(10)	0.954	O	−0.214

Eqn.: $0.9699\ X+0.1021\ Y-0.2442\ Z=0.5836$

Plane (4) defined by C(1), C(2), and C(3)

Pd(1)	−2.385	C(2)	−0.000
C(1)	0.000	C(3)	0.000

Eqn.: $-0.5009\ X-1.4723\ Y+0.8187\ Z=-0.2289$

Plane (5) defined by C(4), C(5), and C(6)

Pd(2)	−2.595	C(5)	0.000
C(4)	0.000	C(6)	−0.000

Eqn.: $0.9844\ X-0.6598\ Y+0.0950\ Z=2.2257$

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[a] X, Y, and Z are co-ordinates in Å referred to the orthorhombic axes.

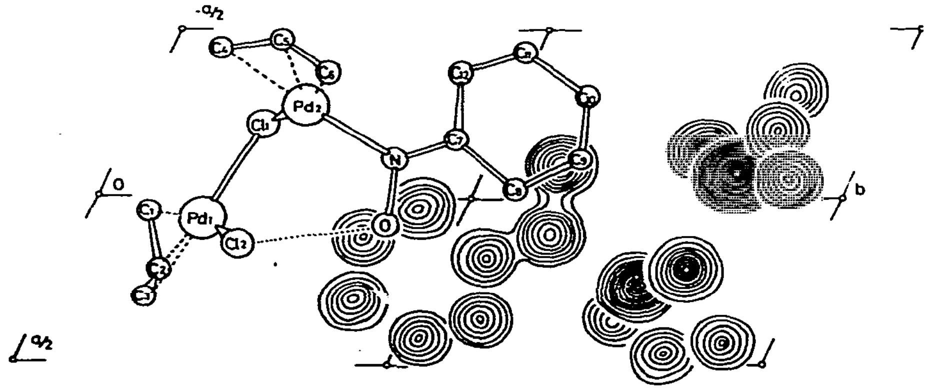

Fig. 1. The projection of the structure on the (001) plane. Contours are drawn at intervals of 1, 2 and 4 e·Å^{-3} for light atoms, chlorine atoms, and palladium atoms respectively, starting at 1 e·Å^{-3}.

the structure on (001) is shown in Fig. 1 and a general view of the molecule in Fig. 2.

The most interesting structural feature in $[Pd(\pi\text{-}C_3H_5)Cl]_2\cdot C_6H_{10}NOH$ for the purpose of this discussion is the mode of the coordination of the oxime to π-allylpalladium chloride. Symmetrical geometry of π-allylpalladium chloride is ruptured by the coordination of the nitrogen of the oxime to one of the palladium atoms; this complex has an unsymmetrical binuclear structure. One of the two palladium atoms,

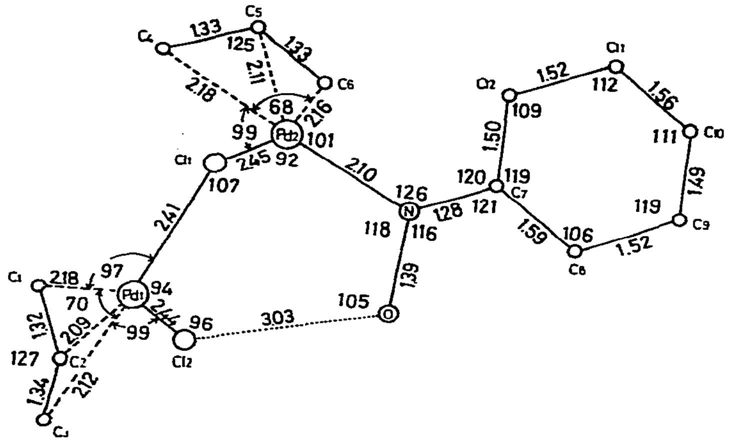

Fig. 2. The general view of the molecule.

Pd(1) is coordinated in a square planar configuration by a π-allyl group and two chlorine atoms. One chlorine atom, a π-allyl group and the nitrogen atom of the oxime complete the square planar coordination of Pd(2). One bridge chlorine atom interconnects the two palladium atoms, the Pd(1)–Cl(1) and Pd(2)–Cl(1) distances being 2.41 Å and 2.45 Å, respectively. The Pd(1)–Cl(1)–Pd(2) angle is 107.3° which is larger than the corresponding angle of 92.1° in bis(π-allylpalladium chloride)[7a]. Another chlorine atom, Cl(2), forms a hydrogen bond with hydroxyl group of the oxime, the Cl(2)–O distance being 3.03 Å. The strong absorption at 3170 cm^{-1} in IR spectrum also suggests the presence of the hydrogen bond. Such a hydrogen bond has been reported in other oxime–palladium chloride complexes. The nonbonding distance between Cl(2) and Pd(2) is 3.33 Å. The orientation of each π-allyl group with respect to the palladium atom resembles those found in other allyl complexes. The mean distance of 2.14 Å of the carbon atoms of the π-allyl groups from the palladium is in good agreement with corresponding value found in $[(C_3H_5)PdCl]_2$[7], and there is some tendency that the terminal carbon atoms are somewhat longer than the central carbon atom, although each of carbon–palladium distances shows slight difference as shown in Table 3. However, as Churchill and O'Brien[8] had once mentioned, the report of Oberhansli and Dahl[7b] that the terminal carbon atoms are somewhat longer than the central carbon atom found in $[(C_3H_5)PdCl]_2$ was not substantiated by a low-temperature study of the same compound[7a]. It should also be remembered that the bond distances between given atom pairs differ slightly in length because of no imposed crystallographic symmetry and thus no idealized point-group symmetry in this complex. The mean carbon–carbon bond length of 1.33 Å and the mean bond angle of 126.0° in the π-allyl group are similar to the corresponding ones observed in $[(C_3H_5)PdCl]_2$[7b]. Two planes of the allyl groups defined by C(1)–C(2)–C(3) and C(4)–C(5)–C(6) are inclined at the angles of 125° and 119° to the palladium coordination planes defined by Pd(1)–Cl(1)–Cl(2) and Pd(2)–Cl(1)–N, respectively. These values are not greatly different from corresponding ones of 111.5° in $[(C_3H_5)PdCl]_2$[7a], 123° and 127° in $[(C_5H_9)PdCl]_2$[9], and 116° in $[PdCl(methallyl)PPh_3]$[10].

The Pd(2)–N bond distance of 2.10 Å agrees well with the value of 2.08 Å in

$PdCl_2(C_6H_{10}NOH)_2$[2]. It is, however, longer than the lengths of 2.031 Å in bis(*N*-isopropyl-3-ethylsalicylaldiminato)palladium[11], and 2.030 Å and 2.043 Å in bis-(ethylenediamine)palladium chloride[12]. The configuration of the cyclohexane ring is also close to that found in $PdCl_2(C_6H_{10}NOH)_2$[2]. The ring takes a chair form and the C–C bond lengths and bond angles are normal. The atoms, C(7), C(8), C(12), and N are almost coplanar, and this coplanarity is due to the double bond character of the C(7)–N bond (1.28 Å). There are no intermolecular contacts significantly shorter than the sum of the van der Waals radii of the participating atoms.

This unsymmetrical binuclear complex is preferred as an intermediate in the ligand exchange reaction of π-allyl complexes to form monomeric complexes.

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